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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>H01L</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 97/11482</b> <b>(43) International Publication Date:</b> 27 March 1997 (27.03.97)
<b>(21) International Application Number:</b> PCT/US96/14054 <b>(22) International Filing Date:</b> 3 September 1996 (03.09.96) <b>(30) Priority Data:</b> 524,296 5 September 1995 (05.09.95) US <b>(71) Applicant:</b> LSI LOGIC CORPORATION [US/US]; 1551 McCarthy Boulevard, Milpitas, CA 95035 (US). <b>(72) Inventors:</b> HEINE, David; 114 Castlewood Drive, Pleasanton, CA 94566 (US). CATABAY, Wilbur, G.; 936 Pomeroy Avenue, Santa Clara, CA 95051 (US). <b>(74) Agent:</b> SCHNECK, Thomas; Law Offices of Thomas Schneck, P.O. Box 2-E, San Jose, CA 95109-0005 (US).		<b>(81) Designated State:</b> JP.  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> REMOVAL OF HALOGENS AND PHOTORESIST FROM WAFERS  <b>(57) Abstract</b>  Method and apparatus for removal of remaining photoresist material and halogen residues (9) after etching from a polysilicon or metallized wafer (15, 35, 55). Exposed portions of the wafer substrate (8), not covered by photoresist material, are etched by exposing the wafer to a first, halogen-containing plasma (PS1), such as HBr or $C_mH_nBr_{2m+2-n}$ for a first selected time interval. The wafer is exposed to a second plasma (PS2), containing $H_2O$ as the primary constituent, for a selected second time interval. Optionally, this second plasma may also contain $O_2$ , $H_2$ , OH and/or $H_2O_2$ as another constituent. Hydrogen radicals and other radicals interact with the remaining photoresist material and with any free halogen and halogen-containing molecules on the wafer to produce reaction products that are removed from the wafer. Each plasma (22, 44, 62, 64) is maintained as an approximately planar body by imposing a time-varying magnetic field and, optionally, a time-varying electrical field on the plasma in directions approximately perpendicular to an exposed surface of the wafer. The processes of etching and of removal of photoresist and halogen residues may be carried out in two separate chambers (11, 31) or in a single chamber (51), with the wafer being maintained in different temperature ranges for the two processes.		

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## REMOVAL OF HALOGENS AND PHOTORESIST FROM WAFERS

Field of the Invention

5 This invention relates to semiconductor processing, and more particularly to removal of residues of photoresist and halogen molecules from a metal or polysilicon surface after photoresist stripping.

Background of the Invention

Masking of a surface on a semiconductor wafer with photoresist is commonly performed to define traces or lines on the surface for  
1 0 subsequent formation of current traces and components. After formation of these traces and/or components, the remaining photoresist material is often removed by exposure to a plasma or to a solution of  $\text{H}_2\text{O}_2$  and sulfuric acid that, ideally, will not significantly etch or otherwise remove  
1 5 the current traces or components or the underlying substrate. Starting materials used for formation of this plasma can include  $\text{O}_2$ ,  $\text{CF}_4$ ,  $\text{H}_2\text{O}$  and other gaseous compounds that react with and remove the photoresist material without seriously degrading other exposed substances on the wafer. A plasma that uses a mixture of  $\text{O}_2$  and  $\text{CF}_4$  will remove the  
2 0 photoresist material at practical rates at relatively low temperatures, and the fluorine atoms and ions in the plasma may partially displace any chlorine present in the photoresist material to thereby reduce the possibility of corrosion on metal surfaces. However, an  $\text{O}_2 + \text{CF}_4$  plasma will also significantly etch an underlying Si-containing substrate materials such as polysilicon,  $\text{SiO}_2$  or  $\text{SiN}$ .

2 5 Another concern is corrosion of a wafer's metal surfaces, for example, an Al alloy, by chlorine-containing compounds such as  $\text{Cl}_2$  and  $\text{AlCl}_3$ . These chlorine-containing residues may be left on the sidewalls of the remaining photoresist and/or metal and, in the presence of moisture, may produce acids such as  $\text{HCl}$  that move to and corrode exposed metal  
3 0 surfaces. Examples of this corrosion process and its control are discussed by Cameron and Chambers in "Successfully Addressing Post-etch Corrosion," Semiconductor International, May 1989, where the presence of a variety Cl-containing compounds, such as  $\text{Al}(\text{OH})_3$ ,  $\text{AlCl}_4^-$  and  $\text{AlCl}_3$

can promote corrosion. One (24-hour) test of effectiveness of suppression of corrosion after a metal etch exposes the etched and non-passivated wafer to clean, ambient air for 24 hours. If no substantial corrosion is observed after 24 hours, the corrosion-suppression process is assumed to be reasonably effective. Unfortunately, use of a fluorine-containing plasma, such as  $O_2 + CF_4$ , for photoresist removal does not always remove all the halogens..

Other plasma starting materials, such as  $O_2$  or  $O_2 + H_2O$ , have also been used for photoresist stripping. Where an  $O_2$  plasma is used for this purpose, stripping activity increases with the concentration of O atoms (and ions) present, and increases with any decrease in activation energy for hydrogen extraction from the base polymer in the photoresist. Fujimura et al, in the 1990 Dry Process Symposium, pp. 153-156, and in Jour. Vac. Sci. Technol., vol. 9B (1991) pp. 357-361, report some interesting results here, where photoresist material is to be removed. The activation energy for H extraction is about 0.52 electron volts equivalent ("ev") where a pure  $O_2$  plasma is used and is about 0.39 ev where an  $O_2 + H_2O$  plasma or an  $O_2 + H_2$  plasma is used for photoresist stripping. Further, the relative concentration of O atoms in the plasma (about 0.5 if only  $O_2$  is used) increases monotonically to about 1.0 if 1-10 percent of  $H_2O$  is added to the plasma, and the relative concentration of O atoms decreases monotonically for further increases in the relative amount of  $H_2O$  added to the plasma. The authors speculate that presence of OH radicals is responsible for much of these effects. In these reports, an  $O_2 + H_2O$  plasma or an  $O_2 + H_2$  plasma is used only for stripping the remaining photoresist material.

Other workers have reported on use of  $H_2$ ,  $O_2$  or  $NH_3$  for control or removal of chlorine or fluorine in semiconductor processes. Schachameyer et al, in U.S. Patent No. 4,940,505, discloses a process for removal of a regrown native oxide layer and a fluorinated layer, formed during epitaxial crystal growth in the presence of fluorine, from a semiconductor wafer. Hydrogen gas is introduced into a reaction chamber containing the wafer, and pulsed excimer laser radiation is directed at the wafer surface(s) through this gas. The incident radiation removes the

fluorine layer and promotes bonding of atoms of the hydrogen gas with silicon to form a substitute layer.

United States Patent No. 5,200,031, issued to Latchford et al, discloses a method for removal of photoresist material from a metal layer on a wafer that removes or inactivates chlorine residues at the same time. In the photoresist removal process,  $\text{NH}_3$  plasma is first flowed through a reaction chamber containing the wafer. A second plasma, containing at least 90 percent  $\text{O}_2$  and at most 10 percent  $\text{NH}_3$ , is then flowed through the chamber for 30-300 sec to complete the photoresist removal process. The 24-hour test was applied, and no remaining photoresist material or corrosion was found on the wafers tested.

A method for photoresist removal from a metal surface on a semiconductor wafer that removes or inactivates chlorine residues is disclosed by Rhoades in U.S. Patent No. 5,221,424. A first stripping step uses a plasma containing  $\text{O}_2$ ,  $\text{C}_m\text{H}_n\text{F}_{2m+2-n}$  ( $m \geq 1$ ;  $n \geq 0$ ) or  $\text{O}_2 + \text{N}_2$ , with a power level of 500-5,000 Watts for an exposure time of 10 - 20 sec. A second stripping step uses a plasma containing  $\text{H}_2\text{O} + \text{H}_2\text{O}_2$  for an exposure time of 30 - 240 sec, with a reaction chamber temperature  $T = 245^\circ\text{C}$  or higher. The 24-hour test was applied, and no chlorine residues were observed on the metal surface(s) from which the photoresist was removed. The inventor does not indicate if all fluorine residues were also removed by this method.

United States Patent No. 5,269,878, issued to Page et al, discloses a metal patterning method for IC fabrication that uses steam to remove chlorine residues after the etch step. Steam, or steam and water in the form of a mist, maintained at a temperature  $T > 100^\circ\text{C}$  is directed at the photoresist material and metallized wafer surface, which are spun at rates of 50 - 1,000 rpm, then at 2,000 - 5,000 rpm. No times are given for application of the steam/water to the photoresist material.

Numasawa, in U.S. Patent No. 5,306,672, discloses a method for forming a gate oxide film, using treatment of the substrate with an HF solution as part of the process, and subsequent removal of fluorine residues. The substrate is treated with hydrofluoric acid, then with HF gas,

then with high purity H<sub>2</sub> gas, maintained at a temperature T  $\geq$  200 °C, to remove any residues of fluorine that remain on the substrate.

A process for simultaneous removal of photoresist and polysilicon etch residues from an IC structure is disclosed by Hills et al in U.S. Patent No. 5,382,316. A polysilicon substrate, with photoresist material applied and maintained at a temperature T = 100 - 400 °C, is exposed to a plasma containing (1) O<sub>2</sub> and/or water vapor and (2) a fluorine-containing etchant gas for a time interval of 30 - 300 sec. This simultaneously removes the (remaining) photoresist material and etch residues such as SiBr<sub>x</sub>, SiCl<sub>y</sub> and silicon oxides.

In U.S. Patent No. 5,399,236, Ha et al disclose formation of a photoresist pattern on an Al metal layer by etching with plasma containing Cl. Residual Cl is then eliminated using an oxygen plasma containing an alkyl ketone or alkyl ether to suppress subsequent corrosion of the wafer.

Other workers have focused on production and maintenance of a plasma with adequate electron-ion energy transfer in a low pressure environment. J.B. Carter et al, in "Transformer Coupled Plasma Etch Technology for the Fabrication of Sub-half micron Structures," Journal of Vacuum Technology Conference (1992), note that, at pressures above 100 milliTorr, the mean free paths for reactants and for products in a plasma are small compared with the dimensions of the plasma sheath so that a representative ion may experience many ion-neutral collisions within the sheath before the ion reaches a substrate that is the target of the ions. These ion-neutral collisions cause a loss of ion energy and, more importantly, a loss in ion directionality that degrades the desired anisotropy of the ion bombardment of the substrate. The effects on the substrate of loss of ion bombardment anisotropy can be minimized by incorporation of special chemicals to create and maintain sidewall passivation or by reducing the pressure and thus increasing the mean free paths for ion-neutral collisions.

However, reduction of these mean free paths may substantially increase the rate of ion energy transfer to the reactor chamber walls, and the reactants must be produced and introduced into the reactor chamber at

correspondingly increased rates. Microwaves have been used with particular uniform magnetic field configurations to create regions of electron cyclotron resonance with locally increased ion density regions. [citations] This approach requires maintenance of stable, uniform magnetic fields, with increased cost and complexity. Another approach, also expensive, uses inductively coupled plasma sources to produce higher density ion sources at low pressures.

Use of a transformer coupled plasma (TCP) to produce a higher density, low pressure plasma reactor region for plasma etching and fabrication of half-micron semiconductor structures is disclosed by Ogle in U.S. Patent No. 4,948,458 and is discussed by Carter et al, op. cit. A plasma reaction chamber is provided with a dielectric window of quartz,  $\text{Al}_2\text{O}_3$  or other suitable non-absorbing material on one wall, and a planar spiral coil is located outside the chamber adjacent to this window. A polysilicon wafer is positioned within the chamber about 3-15 cm from and parallel to this window, and a low pressure ( $p = 1\text{-}3$  milliTorr), chlorine-containing gas is admitted into the chamber. Alternating current flow in the coil produces a 13.56 MHz magnetic field, directed approximately perpendicular to the plane of the coil, in the gas-filled region between the window and the wafer. A low pressure plasma, moving approximately in a collection of planes parallel to the plane of the window, is produced for (preferably anisotropic) etching of small structures in the wafer. Optionally, an alternating electrical field, of frequency  $f = 400\text{-}550$  kHz or around 13.56 MHz, can be applied to an electrically conducting wafer support to provide an electrical field component perpendicular to the wafer plane, to provide an ion velocity component in this direction. The electrical field produced by the wafer support and the magnetic field produced by the planar coil have no particular frequency or phase relationship to each other. Ogle, in U.S. Patent No. 5,277,751, provides further improvements in the TCP apparatus that allow production of an approximately uniform magnetic field over a region up to 30 cm in diameter and allow operation at pressures as low as 0.1 Pascal.

Chen et al, in U.S. Patent Nos. 5,226,967 and 5,368,710, disclose an improvement in the TCP apparatus in which the dielectric window thickness is greater in a central portion of the window than near the window edges, to decrease the induced electrical field within the reaction chamber near this central portion.

Most of these methods focus on removal of photoresist material and chlorine-containing residues from a patterned and etched substrate. What is needed is a method for removing photoresist material and halogen-containing residues, such as SiBr and HBr, from an etched substrate using a TCP source. Preferably, substrate etching and removal of the photoresist and halogen residues should occur in the same reaction chamber.

#### Summary of the Invention

These needs are met by the invention, which provides a method for removal of halogen and photoresist residues from a polySi or metallized wafer during photoresist stripping, using an H<sub>2</sub>O plasma. The wafer temperature for removal of the photoresist and halogen residues is relatively high here, preferably in the range  $T = 180 - 290^{\circ}\text{C}$ .

The photoresist and halogen residues are removed by exposure of the wafer to a plasma containing H<sub>2</sub>O and, optionally, H<sub>2</sub>, O<sub>2</sub>, OH and/or H<sub>2</sub>O<sub>2</sub>, where the wafer temperature is maintained in the range  $T = 180 - 290^{\circ}\text{C}$ . The exposure time for the remaining photoresist material can vary from 30 - 300 sec, and the power applied to create the plasma to remove this material can vary from 1 - 500 Watts, depending in part upon the size of the reaction chamber. This photoresist/halogen residue removal process is performed in a TCP reaction chamber embodiment.

In another embodiment, the etching process and the photoresist/halogen residue removal process are carried out in the same chamber, and the substantially different temperature requirements for each process are met by special wafer temperature control methods.

#### Brief Description of the Drawings

Figure 1 is a schematic side view of a portion of the substrate after the etching process is completed.



Figures 2 and 5 are cross-sectional side views of apparatus suitable for practising the invention in two embodiments.

Figure 3 is a perspective view of the Figure 2 apparatus embodiment.

5 Figure 4 is a graphical view of variation of ideal wafer temperature with time for the removal of substrate (etching) and for the removal of photoresist and halogen residues.

Figure 6 is a cross-sectional side view of wafer support/chuck apparatus suitable for use with the reaction chamber shown in Figure 5.

10 Figures 7 and 8 are flow charts of processes for photoresist stripping and photoresist/halogen residue removal according to the invention.

#### Detailed Description of the Invention

The process of this invention may be utilized in fabrication of an  
15 integrated circuit structure or any other structure where bromine or other halogen residues are likely to remain on the structure after initial processing. Assume, for purposes of illustration, that the structure is a semiconductor wafer that has undergone photoresist deposit, radiation patterning and removal of selected portions of the photoresist material.  
20 Exposed substrate is etched, and the remaining photoresist material must be removed from the wafer, positioned in a plasma reaction chamber. Figure 1 schematically illustrates, in side view, portions of the substrate 8 and photoresist material 9 that remain after etching, before removal of the remaining photoresist material and any halogen-containing residues.

25 Figure 2 is a schematic side view of a plasma reaction chamber 10, which includes a closed housing 11 with a dielectric window 13 located on one wall thereof and which contains a semiconductor wafer 15 supported by a wafer support 17 within this chamber. The dielectric window material is substantially transparent to electromagnetic radiation with a  
30 frequency  $f_{1,0}$  in the range 0.1 - 100 MHz. The dielectric window 13 is preferably heated by a heater 20 to remove most or all of the plasma and/or reaction by-products that would otherwise deposit or otherwise settle on this window. An approximately planar, current-carrying coil 19,

attached to an rf current source 21, is located outside the chamber 10, adjacent to and approximately parallel to the plane of the dielectric window 13. Circulation of a current in the planar coil 19 produces a magnetic field vector  $\underline{B}_{p1}(t)$  approximately normal to the plane of the coil and an associated electrical field  $\underline{E}_{p1}(t)$ .

A first plasma gas source or reservoir 23 introduces a first plasma source gas PS1, containing a hydrated halogen, such as HBr and/or  $C_mH_nBr_{2m+2-n}$  ( $m \geq 1$ ;  $n = 0, 1, \dots, 2m+2$ ), for removal of selected portions of the substrate 8 (Figure 1) on the wafer 15. The plasma gas PS1 used for the substrate removal process in Figure 2 may contain other hydrated halogen molecules, such as HF, HCl, HI,  $C_mH_nF_{2m+2-n}$ ,  $C_mH_nCl_{2m+2-n}$  and/or  $C_mH_nI_{2m+2-n}$ , in place of or in addition to the bromine-containing molecules. An electrical current  $I_{p1}(t)$  varying with time  $t$  and containing an alternating component is applied to the planar coil 19 by the current source 21. The resulting current  $I_{p1}(t)$  in the planar coil 19 may vary with time  $t$  as

$$I_{p1}(t) = I_{p1,0} + I_{p1,1} \cos \omega_{1,0}t, \quad (1)$$

where  $I_{p1,0}$  and  $I_{p1,1}$  are selected constants, with  $I_{p1,1} \neq 0$ , and  $f_{1,0} = \omega_{1,0}/2\pi$  is a selected frequency in the range 0.1 - 100 MHz. Optionally, the wafer support 17 is an electrode with an applied electrical potential

$$V_{s1}(t) = V_{s1,0} + V_{s1,1} \cos (\omega_{1,1}t + \phi_1) \quad (2)$$

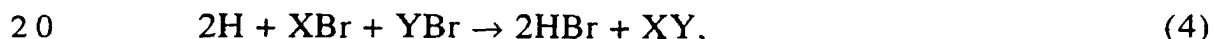
produced by an electrical field source 18, where  $V_{s1,0}$ ,  $V_{s1,1}$  and  $\phi_1$  are selected constants and  $f_{1,1} = \omega_{1,1}/2\pi$  is a selected frequency in the range 0.1 - 100 MHz. That is, the wafer support 17 may be a standard wafer chuck or may be an electrostatic or electrodynamic chuck to which a constant or time-varying electrical potential is applied. The frequencies  $\omega_{1,0}$  and  $\omega_{1,1}$  for the current  $I_{p1}(t)$  and applied electrical potential  $V_{s1}(t)$  may be chosen independently or may be approximately equal to each other. The electromagnetic field produced by the planar coil 19 in the gap between the window 13 and the wafer 15 produce a plasma 22 and help to confine most of this plasma to an approximately planar region that is adjacent to and approximately parallel to one or more of the exposed surfaces of the wafer 15.

- The first plasma source gas PS1 is admitted into the reaction chamber 10 at a partial pressure  $p_1 = 0.5 - 100$  mTorr, the current  $I_{p1}(t)$  is applied to the planar coil 19, and a plasma 22 is formed at a location adjacent to one or more exposed surfaces of the wafer 15. Entry of the plasma source gas PS1 into the chamber 10 from the plasma gas source or reservoir 23 is controlled by a plasma gas valve 23V. For purposes of illustration, the plasma gas used in the etching process will be assumed to include a compound containing H and Br, such as HBr and/or  $C_mH_nBr_{2m+2-n}$  ( $m \geq 1$ ;  $n = 0, 1, \dots, 2m+2$ ). The plasma 22 is at least partially decomposed into H radicals, Br radicals and HBr ions, and these plasma products react with the exposed substrate material. After these reactions occur, the plasma gas 22 and the reaction products are removed from the chamber at a gas exit port 25 that is controlled by an exit port valve 25V.
- Optionally, after the plasma gas 22 and the reaction products have been removed from the chamber 10, a relatively inert purge gas, such as  $N_2$ , He, Ne or Ar, is admitted into the chamber 10 from a purge gas source or reservoir 29 that is controlled by a purge gas valve 29V. The purge gas then exits from the chamber 10 through the exit port 25, carrying away most or all of the residual gases from etching in the reaction chamber 10. The wafer 15 is then moved to a second reaction chamber 30, which is also shown in Figure 1 and is similar to the first reaction chamber 10, for removal of the residual halogens and remaining photoresist material.
- The second reaction chamber 30 includes a housing 31, a dielectric window 33 (preferably heated) and a wafer support 37 for a wafer 35. A planar, current-carrying coil 39, located outside the housing and adjacent to the dielectric window 33, is fed by an rf current source 41 and produces an magnetic field vector  $\underline{B}_{p2}(t)$  directed approximately normal to the plane of the coil and an associated electric field  $\underline{E}_{p2}(t)$  in the region between the dielectric window 33 and the wafer 35, where a plasma will be formed. The current carried in in planar coil 39 preferably has the form

$$I_{p2}(t) = I_{p2,0} + I_{p2,1} \cos \omega_{2,0} t, \quad (3)$$

where  $I_{p2,0}$  and  $I_{p2,1}$  are selected constants, with  $I_{p2,1} \neq 0$ , and  $f_{2,0} = \omega_{2,0}/2\pi$  is a selected frequency in the range 0.1 - 100 MHz. The wafer support 37 is a standard wafer chuck or an electrostatic chuck. Preferably, no applied electrical potential analogous to  $V_{s1}(t)$  in Eq. (2) is applied during removal of the remaining photoresist material and halogen residues in the reaction chamber 30.

A plasma gas source or reservoir 47, controlled by a plasma source valve 47V, introduces a plasma source gas PS2 into the second reaction chamber 30 at a partial pressure  $p_2 = 100 - 2500$  mTorr (preferably in the range 1000-1200 mTorr), and a plasma 44 is formed adjacent to one or more exposed surfaces of the wafer 35, for removal of the residues of photoresist material and residues of the halogen-containing molecules. The plasma source gas PS2 contains  $H_2O$  and, optionally, contains  $O_2$  and/or  $H_2$  and/or  $OH$  and/or  $H_2O_2$  as well. The plasma 44 contains some H radicals,  $H_2$  ions, O radicals,  $O_2$  ions and/or OH radicals. These molecules react with the remaining Br-containing (or halogen-containing) molecules on or near the exposed surfaces of the wafer 35 (Figure 1) to remove these Br molecules by reactions such as



where X and Y may be monovalent elements or molecules. After these reactions occur, the plasma 44 and the reaction products, such as HBr and XY, are removed from the chamber at a gas exit port 45, controlled by a gas exit port valve 45V. The gas exit port 25 and the gas exit port 45 may be independently located on a side wall or on an end wall of their respective housings 11 and 31. Optionally, a purge gas is again introduced into the second reaction chamber 30 to scavenge and carry away any residual gaseous products remaining in the chamber.

Figure 3 is a perspective view showing several of the components of the reaction chamber 10, preferably a LAM TCP chamber, and the reaction chamber 30, preferably a LAM DSQ chamber, that appear in Figure 2.

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Two separate reaction chambers 10 and 30 can be used for removal of exposed substrate and removal of remaining photoresist material and residual halogens. The preferred wafer temperature for removal of polysilicon or metallized substrate (process 1: etching) is in the range  $T \approx T_1 = 0 - 70^\circ\text{C}$ , and the preferred wafer temperatures for removal of photoresist/halogen residues (process 2) is in the range  $T \approx T_2 = 180 - 290^\circ\text{C}$ , as illustrated in Figure 4. The second reaction chamber 30 in Figure 2 must be provided with additional wafer heating or wafer temperature control means for maintaining the wafer temperature at the higher temperatures during the second removal process. An etching molecule such as HCl has a higher vapor pressure than an etching molecule such as HBr at the same temperature so that the wafer temperature used for removal of HCl from the wafer may be lower than the wafer temperature used for removal of HBr.

In an alternative embodiment, a single reaction chamber 50, shown in Figure 5, is used for substrate etching on a wafer 55, purged with a purge gas, used for photoresist/halogen residue removal, and purged with another purge gas. The electrical currents  $I_{p3}(t)$  and  $I_{p4}(t)$  produced in a planar coil 59 are independently selected for the two processes; and an electrical potential fields  $V_{s3}(t)$  is produced in an electrode that is optionally part of a wafer support 57 and used for the etching process.

The reaction chamber 50 in Figure 5 includes a closed housing 51 with a dielectric window 53 (preferably heated by a heater 60) on one wall. A wafer 55 is positioned inside the chamber facing the dielectric window and supported by a grooved or channeled wafer support 57. The wafer support 57 has a plurality of grooves 57G and/or channels 57C formed therein, through which a temperature conditioning ("TC") gas (in the grooves 57G and channels 57C) or liquid (in the channels 57C) is circulated to maintain the wafer temperature within its preferred ranges for each of the etching process and the photoresist/halogen residue removal process. The wafer support 57 is a standard wafer chuck with grooves and channels or, optionally, is an electrostatic or electrodynamic

1 2

wafer chuck with an rf electrical potential field source 58 attached thereto to provide a static or time-varying electrical potential

$$V_{s3}(t) = V_{s3,0} + V_{s3,1} \cos(\omega_{3,1}t + \phi_3) \quad (5)$$

at the wafer support. An approximately planar, current-carrying coil 59 is  
 5 located outside the chamber housing 51, adjacent to and with its plane approximately parallel to, a plane of the dielectric window 53. Current  $I_{p3}(t)$  of the form

$$I_{p3}(t) = I_{p3,0} + I_{p3,1} \cos \omega_{3,0}t, \quad (6)$$

is supplied for the planar coil 59 by an rf current source 61. The  
 1 0 frequencies  $\omega_{3,0}$  and  $\omega_{3,1}$  may be chosen independently or may be approximately equal to each other.

A first plasma gas PS1 from a first plasma gas source or reservoir 63 is admitted to the interior of the chamber 50 through a first plasma source valve 63V, and a first plasma 62 is formed adjacent to one or more  
 1 5 exposed surfaces of the wafer 55. At this point in time, selected portions of the wafer 55 are covered with photoresist material that was not removed in the initial patterning. Exposure of the wafer 55 (selectively covered with photoresist material) to the first plasma gas PS1 removes selected portions of the exposed substrate, through etching. During this etching  
 2 0 process, the wafer 55 is maintained in a first preferred temperature range  $T \approx T1$  by a first TC fluid (liquid or gas) from a first TC fluid source 71 that flows through the grooves 57G (gas only) or through the channels 57C (liquid or gas) in the wafer support 57 to a TC fluid reservoir 73. Circulation of this first TC fluid within the wafer support 57 maintains the  
 2 5 wafer 55 at a relatively low temperature  $T \approx T1$  during etching. The temperature  $T \approx T1$  of the wafer 55 can also be maintained by other means during the etching process.

Optionally, the grooved or channeled wafer support 57 may be replaced by a more conventional solid wafer support, such as 17 or 37 in  
 3 0 Figure 2, and the wafer 55 may be heated to the appropriate temperature range by two or more radiant heating units 76 and 78 that are positioned adjacent to and are directed at the wafer in the etch process and/or in the photoresist/halogen residue removal process, as indicated in Figure 5.

Preferably, the radiant heating units 76 and 78 are isolated from the plasma 62 (or 64) in the reaction chamber 50, as shown in Figure 5, and are positioned to irradiate the wafer 55 through heated dielectric windows 77 and 79, respectively. The radiant heating units are supplied with power  
 5 from a radiant heat energy source 80.

The first plasma gas PS1, selected portions of the substrate material and etch reaction products exit from the reaction chamber 50 through a gas exit port 65 and associated exit port valve 65V, located in a side wall of the housing 51, or through a gas exit port 66 and associated exit port  
 10 valve 66V, located in a bottom wall of the housing 51. A purge gas, such as N<sub>2</sub>, He, Ne or Ar, is optionally introduced into the chamber 50 from a purge gas source 69 and associated purge gas valve 69V and allowed to exit through the gas exit port 65 and/or through the gas exit port 66, to carry away some or all of the etched substrate material and etch reaction  
 15 products.

A second plasma gas PS2 from a second plasma gas source or reservoir 67 is admitted to the reaction chamber 50 through a second plasma source valve 67V, and a second plasma 64 is formed adjacent to one or more of the exposed surfaces of the wafer 55. At this point in time,  
 20 the etched wafer 55, partly covered with photoresist material, resembles the wafer profile shown in Figure 1 and may have halogen residues on the exposed wafer surfaces. During the photoresist/halogen residue removal process, the wafer is maintained in a second preferred temperature range  $T \approx T_2$  by a second TC fluid from a second TC fluid source 75 that flows  
 25 through the grooves 57G (gas only) or channels 57C (liquid or gas) in the wafer support 57 to the fluid reservoir 73. Again, circulation of the second TC fluid within the wafer support 57 can be replaced or supplemented by heating from the radiant heating units 76 and 78, to maintain the wafer temperature in the second preferred temperature range  
 30  $T \approx T_2$ .

Current  $I_{p4}(t)$  of the form

$$I_{p4}(t) = I_{p4,0} + I_{p4,1} \cos \omega_{4,0} t, \quad (7)$$

1 4

is supplied for the planar coil 59 by an rf current source 61. The frequencies  $\omega_{3,0}$  and  $\omega_{4,0}$  may be chosen independently or may be approximately equal to each other. The remaining photoresist material and halogen residues are removed from the surfaces of the wafer 55 by the second plasma 64. This second plasma gas PS2 is preferably  $H_2O$  and may also contain  $H_2$ ,  $O_2$ ,  $OH$  and/or  $H_2O_2$ . Reaction of the second plasma 64 with the residues on the wafer 55 removes the remaining photoresist material and halogen residues from the wafer surfaces. The second plasma gas, remaining photoresist material, halogen residues and reaction products exit from the reaction chamber 50 through the exit port 65 and/or through the exit port 66. The reaction chamber is then purged with a purge gas, such as  $N_2$ ,  $He$ ,  $Ne$  or  $Ar$ , from the purge gas source 69.

Figure 6 illustrates in more detail a wafer support 57 that can be used as part of the invention. The wafer support 57 includes a relatively thin upper wafer support block 57U that optionally contains a plurality of fluid-carrying grooves (interconnected or otherwise) 57G. The wafer support 57 also includes a lower support block 57L that optionally contains a plurality of interconnected fluid-carrying channels 57C. A TC gas optionally flows under some pressure from a first TC gas source 71 through the fluid flow grooves 57G to a fluid reservoir 73. A TC fluid (gas or liquid) optionally flows under some pressure from a TC fluid source 75 through the fluid flow channels 57C to the fluid reservoir 73. The TC gas circulated in the fluid flow grooves 57G is preferably a high specific heat capacity gas, such as  $H_2O$  gas,  $He$ ,  $Ne$  or  $Ar$ , maintained at a relatively low temperature, such as  $T \leq 70^\circ C$ . The TC fluid circulated in the fluid flow channels 57C is preferably a high specific heat capacity fluid, such as deionized water,  $H_2O$  gas,  $He$ ,  $Ne$  or  $Ar$ , maintained at a relatively low temperature, such as  $T \approx T_1 = 0 - 70^\circ C$ .

The upper wafer support block 57U is spaced apart from the lower wafer support block 57L by thermally insulating spacers 57S that define a separation space 57V between the upper wafer support block and the lower wafer support block. The upper support block 57U is preferably a thin block of high thermal conductivity material of relatively low thermal



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mass. The lower support block 57L is preferably a block of high thermal conductivity material of relatively high thermal mass. The relatively low thermal mass of the thin upper support block 57U allows this block to be heated or cooled to a target temperature relatively quickly.

5           The separation space 57V can be alternatingly evacuated or filled with an inert, high thermal conductivity second TC fluid, such as He, Ne or Ar, from a second TC fluid source 74. The separation space 57V is preferably filled with the second TC fluid when a wafer 55 is to be maintained in the lower temperature range  $T \approx T1$  and is preferably  
1 0           evacuated when the wafer is to be maintained in the higher temperature range  $T \approx T2$ .

          In the wafer etching process, the wafer 55 is maintained at a temperature in the range  $T \approx T1 = 0 - 70^\circ\text{C}$ , by circulating a relatively cool first TC fluid in the channels 57C, with the separation space 57V  
1 5           preferably being filled with the third TC fluid.

          In the photoresist/halogen residue removal process, the wafer 55 is maintained at a temperature in the range  $T \approx T2 = 180 - 290^\circ\text{C}$ , by optionally circulating  $\text{H}_2\text{O}$  gas, He or another high temperature gas in the grooves 57G and by evacuating the separation space 57V.

2 0           In a reversed situation, the separation space 57S can be filled with the second TC fluid when the wafer 55 is to be maintained in the lower temperature range  $T \approx T1$ , for etching, and can be evacuated when the wafer is to be maintained in the higher temperature range  $T \approx T2$ , for removal of photoresist material and halogen residue. In this reversed  
2 5           situation, a warm TC fluid ( $T \geq 180^\circ\text{C}$ ) is always circulated through the fluid-carrying channels 57 C in the wafer lower support block 57L; a relatively cool (warm) TC gas is circulated through the gas-carrying grooves 57G in the wafer upper support block 57U during etching (during photoresist/halogen removal).

3 0           Figure 7 illustrates the processes of etching and removal of the remaining photoresist material and halogen residues, using the double chamber apparatus shown in Figure 2. An etchant or substrate removal gas is admitted to a first reaction chamber, in step 81, and an etching plasma is

formed using a planar, current-carrying coil, in step 83. This etchant gas includes halogen-containing molecules, such as HF, HCl, HBr or HI and/or a halogenated hydrocarbon such as  $C_nH_mBr_{2n+2-m}$ . In step 85, a wafer, maintained at a selected temperature in the range  $T \approx T1 = 0 - 70^\circ C$ , with portions of the photoresist material removed as indicated in Figure 1 to expose corresponding portions of the substrate, is exposed to the etching plasma. The planar coil described above is used to confine most of the etching plasma approximately to a plane adjacent to an exposed wafer surface. The etching plasma remains within the reaction chamber long enough so that the exposed substrate is exposed to and reacts with this plasma, to remove selected portions of the exposed substrate. In step 87, the etching reaction products are removed from the reaction chamber and the etching plasma is extinguished. In step 89 (optional), the reaction chamber is flushed with an inert gas, such as  $N_2$ , He, Ne, Ar or another suitable gas, to remove most or all of the etching reaction products produced by plasma reactions with the exposed substrate that has been removed. Preferably, the wafer temperature, wafer exposure time and power applied to form the etching plasma gas in the respective ranges  $T \approx T1 = 0 - 70^\circ C$ ,  $\Delta t = 30 - 300$  sec and  $P = 1 - 500$  Watts. At this point, photoresist material and residues of the halogen-containing molecules used for etching remain on the wafer surfaces.

In step 90, the wafer is transported from the first reaction chamber to a second reaction chamber for removal of the remaining photoresist and halogen residues, where the wafer is maintained at a higher selected temperature ( $T \approx T2 = 180 - 290^\circ C$ ). In step 91, a photoresist/halogen residue removal gas containing  $H_2O$  and, optionally,  $O_2$  and/or  $H_2$  and/or OH and/or  $H_2O_2$ , is admitted to the second reaction chamber. An  $H_2O$  plasma is formed and positioned in step 93, using another planar, current-carrying coil to maintain the plasma approximately in a plane, for removal of the remaining photoresist and halogen residues contained on the wafer surfaces. The wafer is then exposed to the  $H_2O$  plasma, in step 95. This plasma contains a modest fraction of radicals and/or ions of H,  $H_2$ , O,  $O_2$  and/or OH that react with the remaining photoresist material and with

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residual halogen-containing molecules, such as Br or SiBr, on the exposed surfaces of the wafer to form HBr and other bromine-containing molecules, by reactions such as that set forth in Eq. (4) above. The unreacted plasma, photoresist material constituents and residual halogen-containing molecules exit from the second reaction chamber and the plasma is extinguished, in step 97. The second reaction chamber is optionally flushed with an inert gas, such as N<sub>2</sub>, He, Ne or Ar, in step 99, to remove any remaining gas molecules, especially halogen-containing molecules. Preferably, the wafer temperature, wafer exposure time and power applied to form the H<sub>2</sub>O plasma are in the respective ranges  $T \approx T_2 = 180 - 290^\circ\text{C}$ ,  $\Delta t = 30 - 300$  sec and  $P = 1 - 500$  Watts. The wafer can then be moved to its next processing station.

Figure 8 illustrates the etching process and photoresist/halogen residue removal processes using the single reaction chamber apparatus shown in Figure 5. An etching gas, including halogen-containing molecules, such as HF, HCl, HBr or HI and/or a halogenated hydrocarbon such as C<sub>n</sub>H<sub>m</sub>Br<sub>2n+2-m</sub>, is admitted to a reaction chamber, in step 101. An etching plasma is formed using a planar, current-carrying coil, in step 103. In step 105, a wafer, maintained at a selected temperature in the range  $T \approx T_1 = 0 - 70^\circ\text{C}$  and partly coated with photoresist material, is exposed to this etching plasma, using the planar coil as described above to confine most of the plasma approximately to a plane adjacent to an exposed wafer surface. The etching plasma remains within the reaction chamber long enough so that selected portions of the exposed substrate are exposed to and react with this plasma, and these selected portions of the exposed substrate material are removed. In step 107, the etching reaction products are removed from the reaction chamber and the etching plasma is extinguished. In step 109 (optional), the reaction chamber is flushed with an inert gas, such as N<sub>2</sub>, He, Ne, Ar or another suitable gas, to remove most or all of the etching reaction products produced by this plasma. Preferably, the wafer temperature, wafer exposure time and power applied to form the etching plasma gas are in the respective ranges  $T \approx T_1 = 0 - 70^\circ\text{C}$ ,  $\Delta t = 30 - 300$  sec and  $P = 1 - 500$  Watts. In step 110, the

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wafer temperature is elevated to a second temperature range  $T \approx T_2 = 180 - 290^\circ\text{C}$ . The wafer remains in the (single) reaction chamber.

5 In step 111, a photoresist/halogen residue removal gas containing  $\text{H}_2\text{O}$  and, optionally,  $\text{O}_2$  and/or  $\text{H}_2$  and/or  $\text{OH}$  and/or  $\text{H}_2\text{O}_2$ , is admitted to the (same) reaction chamber. An  $\text{H}_2\text{O}$  plasma is formed and positioned in step 113, using another planar, current-carrying coil to maintain the plasma approximately in a plane, for removal of the remaining photoresist material and residual halogen-containing molecules. The wafer surface at this point contains some photoresist material and residues of the halogen-  
10 containing molecules. The wafer is then exposed to the  $\text{H}_2\text{O}$  plasma, in step 115. This plasma optionally contains a modest fraction of radicals and/or ions of  $\text{H}$ ,  $\text{H}_2$ ,  $\text{O}$ ,  $\text{O}_2$  and/or  $\text{OH}$  that react with the remaining photoresist material and with the residual halogen-containing molecules, such as  $\text{Br}$  or  $\text{SiBr}$ , on the surfaces of the wafer to form  $\text{HBr}$ ,  $\text{BrOH}$  and  
15 other bromine-containing molecules, by reactions such as that set forth in Eq. (4) above. The unreacted plasma, photoresist material constituents and residual halogen-containing molecules exit from the reaction chamber and the plasma is extinguished, in step 117. The reaction chamber is again optionally flushed with an inert gas, such as  $\text{N}_2$ ,  $\text{He}$ ,  $\text{Ne}$  or  $\text{Ar}$ , in step  
20 119, to remove any remaining gases. Preferably, the wafer temperature, wafer exposure time and power applied to form the  $\text{H}_2\text{O}$  plasma are in the respective ranges  $T \approx T_2 = 180 - 290^\circ\text{C}$ ,  $\Delta t = 30 - 300$  sec and  $P = 1 - 500$  Watts. The wafer can then be moved to its next processing station.

25 The processes described above can also be used to remove residues containing fluorine and/or chlorine and/or bromine and/or iodine molecules from the wafer. The exposed wafer material may be polysilicon. Alternatively, the exposed wafer material may be metallized with a metal or metal alloy, such as  $\text{Al}$ , where a presence of residue of a halogen such as chlorine can lead to corrosion of the exposed metal.

Claims

1. A method of removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the method comprising the steps of:

providing a wafer, having photoresist material coating and residual halogen-containing molecules on portions of its surface in a reaction chamber;

generating a plasma from a plasma gas that includes  $\text{H}_2\text{O}$  molecules as a constituent, to produce at least one hydrogen-containing radical in the plasma

maintaining the plasma as an approximately planar body that is approximately parallel to an exposed surface of the wafer, by providing a time-varying magnetic field whose magnetic field vector  $\underline{B}_1(t)$  is substantially perpendicular to an exposed surface of the wafer;

exposing the wafer, photoresist material coating and residual halogen-containing molecules to the plasma, to remove substantially all of the photoresist material coating and residual halogen-containing molecules from the wafer; and

removing the gas products from reaction of the plasma with the photoresist material coating and residual halogen-containing molecules from the reaction chamber.

2. The method of claim 1, further comprising the step of providing said plasma gas with a second gas constituent that is drawn from the class hydrogen-containing and oxygen-containing molecules consisting of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{OH}$  and  $\text{H}_2\text{O}_2$ .

3. A method of removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the method comprising the steps of:

providing a wafer, having photoresist material coating on portions of its surface and being exposed on other portions of its surface, in a reaction chamber;

generating a first plasma from a first plasma gas that includes selected molecules containing a selected halogen;

maintaining the first plasma as an approximately planar body that is approximately parallel to an exposed surface of the wafer, by providing a time-varying magnetic field whose magnetic field vector  $\underline{B}_1(t)$  is substantially perpendicular to the wafer exposed surface;

allowing the first plasma to etch selected portions of the wafer at the exposed surfaces of the wafer;

maintaining said wafer in a selected range of temperatures  $T$  with a range  $0^\circ\text{C} \leq T \leq 70^\circ\text{C}$ , while said wafer is exposed to said first plasma;

removing gas products from reaction of the first plasma with the wafer from the reaction chamber;

generating a second plasma from a second plasma gas that includes molecules of  $\text{H}_2\text{O}$  as a primary gas constituent, to produce at least one hydrogen-containing radical in the second plasma in the same reaction chamber;

maintaining the second plasma as an approximately planar body that is approximately parallel to the wafer exposed surface, by providing a time-varying magnetic field whose magnetic field vector  $\underline{B}_2(t)$  is substantially perpendicular to a plane of the wafer exposed surface;

exposing the photoresist material and residual halogen-containing molecules from the first plasma to the second plasma for a time interval of at least 30 seconds, and allowing the hydrogen-containing radicals to react with and remove the photoresist material and the residual halogen-containing molecules on the wafer to remove these residual substances from the wafer;

maintaining said wafer in a selected range of temperatures  $T$  with a range  $180^\circ\text{C} \leq T \leq 290^\circ\text{C}$ , while said wafer is exposed to said second plasma;

removing gas products from reaction of the second plasma with the photoresist material and residual halogen-containing molecules from the reaction chamber.

4. The method of claim 3, further comprising the step of providing said second plasma gas with a second gas constituent that is drawn from the class hydrogen-containing and oxygen-containing molecules consisting of  $H_2$ ,  $O_2$ ,  $OH$  and  $H_2O_2$ .

5. Apparatus for removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the apparatus comprising:

a closed housing having a dielectric window on one wall of the housing that is substantially transparent to electromagnetic radiation having a selected frequency  $f_0$  in the range 0.1 - 100 MHz;

a wafer support, positioned within the housing and adjacent to but spaced apart from the dielectric window, for supporting a wafer having a first portion of its surface covered with photoresist material and having a second portion of its surface exposed;

wafer temperature control means for maintaining the temperature of a wafer that is positioned on the wafer support approximately at a first temperature  $T_1$  in the approximate range  $0\text{ }^{\circ}\text{C} \leq T_1 \leq 70\text{ }^{\circ}\text{C}$  during a first selected time interval and for maintaining the temperature of the wafer approximately at a second temperature  $T_2$  in the approximate range  $180\text{ }^{\circ}\text{C} \leq T_2 \leq 290\text{ }^{\circ}\text{C}$  during a second selected time interval;

a first electromagnetic field source, positioned outside the housing adjacent to the dielectric window, that produces an electromagnetic field with a magnetic field vector  $\underline{B}_p(t)$  that varies with time  $t$  approximately as  $\underline{B}_p(t) = \underline{B}_{p0} + \underline{B}_{p1}\cos(2\pi f_0 t)$  in the first selected time interval and in the second selected time interval, where  $\underline{B}_{p0}$  and  $\underline{B}_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}_p(t)$  is approximately perpendicular to a plane of the dielectric window and where  $f_0$  is a selected frequency lying in the range  $0.1\text{ MHz} \leq f_0 \leq 100\text{ MHz}$ ;

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a second electromagnetic field source, positioned within the housing, that produces an electromagnetic field with an electrical field vector  $\underline{E}_s(t)$  that varies with time approximately as  $\underline{E}_s(t) = \underline{E}_{s0} + \underline{E}_{s1} \cos(2\pi f_1 t + \phi)$  in the first selected time interval, where  $\underline{E}_{p0}$  and  $\underline{E}_{p1}$  are selected constant vectors, where  $f_1$  is a selected frequency lying in the range  $0.1 \text{ MHz} \leq f_1 \leq 100 \text{ MHz}$ , and where  $\phi$  is a selected phase angle;

a first plasma gas source, positioned adjacent to and connected to the housing, to deliver a first selected plasma gas containing a compound including hydrogen and a selected halogen to a selected region within the housing that is positioned between the wafer support and the dielectric window, in a first processing time interval that includes the first selected time interval;

a second plasma gas source, positioned adjacent to and connected to the housing, to deliver a second selected plasma gas containing  $\text{H}_2\text{O}$  to the selected region within the housing in a second processing time interval that includes the second selected time interval; and

an exit port to remove gases from within the housing after completion of the first processing time interval and after completion of the second processing time interval.

6. The apparatus of claim 5, wherein said second selected plasma gas also contains molecules drawn from the class of molecules consisting of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{OH}$  and  $\text{H}_2\text{O}_2$ .

7. Apparatus for removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the apparatus comprising:

a closed first housing having a first dielectric window on one wall of the first housing that is substantially transparent to electromagnetic radiation having a selected frequency  $f_0$  in the range  $0.1 - 100 \text{ MHz}$ ;

a first wafer support, positioned within the first housing and adjacent to but spaced apart from the first dielectric window, for



supporting a wafer having a first portion of its surface covered with photoresist material and having a second portion of its surface exposed;

first wafer temperature control means for maintaining the temperature of a wafer that is positioned on the first wafer support approximately at a first temperature  $T_1$  in the approximate range  $0^\circ\text{C} \leq T_1 \leq 70^\circ\text{C}$  during a first selected time interval;

a first electromagnetic field source, positioned outside the first housing adjacent to the first dielectric window, that produces an electromagnetic field with a magnetic field vector  $\underline{B}_p(t)$  that varies with time  $t$  approximately as  $\underline{B}_p(t) = \underline{B}_{p0} + \underline{B}_{p1}\cos(2\pi f_0 t)$  in the first selected time interval and in the second selected time interval, where  $\underline{B}_{p0}$  and  $\underline{B}_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}_p(t)$  is approximately perpendicular to a plane of the first dielectric window and where  $f_0$  is a selected frequency lying in the range  $0.1\text{ MHz} \leq f_0 \leq 100\text{ MHz}$ ;

a second electromagnetic field source, positioned within the first housing, that produces an electromagnetic field with an electrical field vector  $\underline{E}_s(t)$  that varies with time approximately as  $\underline{E}_s(t) = \underline{E}_{s0} + \underline{E}_{s1}\cos(2\pi f_1 t + \phi)$  in the first selected time interval, where  $\underline{E}_{p0}$  and  $\underline{E}_{p1}$  are selected constant vectors, where  $f_1$  is a selected frequency lying in the range  $0.1\text{ MHz} \leq f_1 \leq 100\text{ MHz}$ , and where  $\phi$  is a selected phase angle;

a first plasma gas source, positioned adjacent to and connected to the first housing, to deliver a first selected plasma gas containing a compound including hydrogen and a selected halogen to a first selected region within the first housing that is positioned between the first wafer support and the first dielectric window, in a first processing time interval that includes the first selected time interval;

a first exit port to remove gases from within the first housing after completion of the first processing time interval;

a second closed housing having a second dielectric window on one wall of the second housing that is substantially transparent to electromagnetic radiation having a selected frequency  $f_0$  in the range  $0.1 - 100\text{ MHz}$ ;

a second wafer support, positioned within the second housing and adjacent to but spaced apart from the second dielectric window, for supporting a wafer having an exposed surface;

second wafer temperature control means for maintaining the temperature of a wafer that is positioned on the second wafer support approximately at a second temperature  $T_2$  in the approximate range  $180^\circ\text{C} \leq T_2 \leq 290^\circ\text{C}$  during a second selected time interval;

a third electromagnetic field source, positioned outside the second housing adjacent to the second dielectric window, that produces an electromagnetic field with a magnetic field vector  $\underline{B}'_p(t)$  that varies with time  $t$  approximately as  $\underline{B}'_p(t) = \underline{B}'_{p0} + \underline{B}'_{p1}\cos(2\pi f_0 t)$  in the second selected time interval, where  $\underline{B}'_{p0}$  and  $\underline{B}'_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}'_p(t)$  is approximately perpendicular to a plane of the second dielectric window and where  $f_0$  is a selected frequency lying in the range  $0.1\text{ MHz} \leq f_0 \leq 100\text{ MHz}$ ;

a second plasma gas source, positioned adjacent to and connected to the second housing, to deliver a second selected plasma gas containing  $\text{H}_2\text{O}$  to a second selected region within the second housing that is positioned between the second wafer support and the second dielectric window in a second processing time interval that includes the second selected time interval; and

a second exit port to remove gases from within the housing after completion of the second processing time interval.

8. The apparatus of claim 7, wherein said second selected plasma gas also contains molecules drawn from the class of molecules consisting of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{OH}$  and  $\text{H}_2\text{O}_2$ .

9. Apparatus for removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the apparatus comprising:

a closed housing having a dielectric window on one wall of the housing that is substantially transparent to electromagnetic radiation having a selected frequency  $f_0$  in the range 0.1 - 100 MHz;

a wafer support, positioned within the housing and adjacent to but spaced apart from the dielectric window, for supporting a wafer having a first portion of its surface covered with photoresist material and having a second portion of its surface exposed;

a plurality of fluid-carrying grooves or channels, formed in the wafer support for wafer temperature control, for maintaining the temperature of a wafer that is positioned on the wafer support approximately at a first temperature  $T_1$  in the approximate range  $0\text{ }^{\circ}\text{C} \leq T_1 \leq 70\text{ }^{\circ}\text{C}$  during a first selected time interval and for maintaining the temperature of the wafer approximately at a second temperature  $T_2$  in the approximate range  $180\text{ }^{\circ}\text{C} \leq T_2 \leq 290\text{ }^{\circ}\text{C}$  during a second selected time interval;

a first electromagnetic field source, positioned outside the housing adjacent to the dielectric window and including a current-carrying coil formed approximately in a plane that is approximately perpendicular to a plane of the dielectric window, that produces an electromagnetic field with a magnetic field vector  $\underline{B}_p(t)$  that varies with time  $t$  approximately as  $\underline{B}_p(t) = \underline{B}_{p0} + \underline{B}_{p1} \cos(2\pi f_0 t)$  in the first selected time interval and in the second selected time interval, where  $\underline{B}_{p0}$  and  $\underline{B}_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}_p(t)$  is approximately perpendicular to a plane of the dielectric window and where  $f_0$  is a selected frequency lying in the range  $0.1\text{ MHz} \leq f_0 \leq 100\text{ MHz}$ ;

a second electromagnetic field source, positioned within the housing adjacent to the wafer support and including a time-varying voltage source, that produces an electromagnetic field with an electrical field vector  $\underline{E}_s(t)$  that varies with time approximately as  $\underline{E}_s(t) = \underline{E}_{s0} + \underline{E}_{s1} \cos(2\pi f_1 t + \phi)$  in the first selected time interval, where  $\underline{E}_{p0}$  and  $\underline{E}_{p1}$  are selected constant vectors, where  $f_1$  is a selected frequency lying in the range  $0.1\text{ MHz} \leq f_1 \leq 100\text{ MHz}$ , and where  $\phi$  is a selected phase angle;

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a first plasma gas source, positioned adjacent to and connected to the housing, to deliver a first selected plasma gas containing a compound including hydrogen and a selected halogen to a selected region within the housing that is positioned between the wafer support and the dielectric window, in a first processing time interval that includes the first selected time interval;

a second plasma gas source, positioned adjacent to and connected to the housing, to deliver a second selected plasma gas containing  $H_2O$  to the selected region within the housing in a second processing time interval that includes the second selected time interval; and

an exit port to remove gases from within the housing after completion of the first processing time interval and after completion of the second processing time interval.

10. Apparatus for removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the apparatus comprising:

a closed first housing having a first dielectric window on one wall of the first housing that is substantially transparent to electromagnetic radiation having a selected frequency  $f_0$  in the range 0.1 - 100 MHz;

a first wafer support, positioned within the first housing and adjacent to but spaced apart from the first dielectric window, for supporting a wafer having a first portion of its surface covered with photoresist material and having a second portion of its surface exposed;

a plurality of fluid-carrying grooves or channels, formed in the first wafer support for wafer temperature control, for maintaining the temperature of a wafer that is positioned on the first wafer support approximately at a first temperature  $T_1$  in the approximate range  $0^\circ C \leq T_1 \leq 70^\circ C$  during a first selected time interval;

a first electromagnetic field source, positioned outside the first housing adjacent to the first dielectric window and including a current-carrying coil formed approximately in a plane that is approximately perpendicular to a plane of the dielectric window, that produces an

electromagnetic field with a magnetic field vector  $\underline{B}_p(t)$  that varies with time  $t$  approximately as  $\underline{B}_p(t) = \underline{B}_{p0} + \underline{B}_{p1}\cos(2\pi f_0 t)$  in the first selected time interval and in the second selected time interval, where  $\underline{B}_{p0}$  and  $\underline{B}_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}_p(t)$  is approximately perpendicular to a plane of the first dielectric window and where  $f_0$  is a selected frequency lying in the range  $0.1 \text{ MHz} \leq f_0 \leq 100 \text{ MHz}$ ;

a second electromagnetic field source, positioned within the first housing adjacent to the first wafer support and including a time-varying voltage source, that produces an electromagnetic field with an electrical field vector  $\underline{E}_s(t)$  that varies with time approximately as  $\underline{E}_s(t) = \underline{E}_{s0} + \underline{E}_{s1}\cos(2\pi f_1 t + \phi)$  in the first selected time interval, where  $\underline{E}_{p0}$  and  $\underline{E}_{p1}$  are selected constant vectors, where  $f_1$  is a selected frequency lying in the range  $0.1 \text{ MHz} \leq f_1 \leq 100 \text{ MHz}$ , and where  $\phi$  is a selected phase angle;

a first plasma gas source, positioned adjacent to and connected to the first housing, to deliver a first selected plasma gas containing a compound including hydrogen and a selected halogen to a first selected region within the first housing that is positioned between the first wafer support and the first dielectric window, in a first processing time interval that includes the first selected time interval;

a first exit port to remove gases from within the first housing after completion of the first processing time interval;

a second closed housing having a second dielectric window on one wall of the second housing that is substantially transparent to electromagnetic radiation having a selected frequency  $f_0$  in the range  $0.1 - 100 \text{ MHz}$ ;

a second wafer support, positioned within the second housing and adjacent to but spaced apart from the second dielectric window, for supporting a wafer having an exposed surface;

a plurality of fluid-carrying grooves or channels, formed in the second wafer support for wafer temperature control, for maintaining the temperature of a wafer that is positioned on the second wafer support

approximately at a second temperature  $T_2$  in the approximate range  $180^\circ\text{C} \leq T_2 \leq 290^\circ\text{C}$  during a second selected time interval;

a third electromagnetic field source, positioned outside the second housing adjacent to the second dielectric window and including a current-carrying coil formed approximately in a plane that is approximately perpendicular to a plane of the second dielectric window, that produces an electromagnetic field with a magnetic field vector  $\underline{B}'_p(t)$  that varies with time  $t$  approximately as  $\underline{B}'_p(t) = \underline{B}'_{p0} + \underline{B}'_{p1} \cos(2\pi f_0 t)$  in the third selected time interval and in the fourth selected time interval, where  $\underline{B}'_{p0}$  and  $\underline{B}'_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}'_p(t)$  is approximately perpendicular to a plane of the dielectric window and where  $f_0$  is a selected frequency lying in the range  $0.1 \text{ MHz} \leq f_0 \leq 100 \text{ MHz}$ ;

a second plasma gas source, positioned adjacent to and connected to the second housing, to deliver a second selected plasma gas containing  $\text{H}_2\text{O}$  to a second selected region within the second housing that is positioned between the second wafer support and the second dielectric window in a second processing time interval that includes the second selected time interval; and

a second exit port to remove gases from within the housing after completion of the second processing time interval.

11. A system for removal of photoresist material from a polysilicon or metallized semiconductor wafer on which the photoresist has been deposited, the system comprising:

a wafer support for supporting a wafer having an exposed surface;  
 wafer temperature control means for maintaining the temperature of a wafer that is positioned on the wafer support approximately at a first temperature  $T_1$  in the approximate range  $0^\circ\text{C} \leq T_1 \leq 70^\circ\text{C}$  during a first selected time interval and for maintaining the temperature of the wafer approximately at a second temperature  $T_2$  in the approximate range  $180^\circ\text{C} \leq T_2 \leq 290^\circ\text{C}$  during a second selected time interval;

an electromagnetic field source that produces an electromagnetic field with a magnetic field vector  $\underline{B}_p(t)$  that varies with time  $t$  approximately as  $\underline{B}_p(t) = \underline{B}_{p0} + \underline{B}_{p1} \cos(2\pi f_0 t)$ , where  $\underline{B}_{p0}$  and  $\underline{B}_{p1}$  are selected constant vectors, where the direction of the magnetic field  $\underline{B}_p(t)$  is approximately perpendicular to the wafer exposed surface, where  $f_0$  is a selected frequency lying in the range  $0.1 \text{ MHz} \leq f \leq 100 \text{ MHz}$ ;

a first plasma gas source to deliver a selected first plasma gas containing a compound including hydrogen and a halogen to a selected region adjacent to the wafer exposed surface in the first selected time interval;

a second plasma gas source to deliver a selected second plasma gas containing  $\text{H}_2\text{O}$  to the selected region in the second selected time interval; and

exit means for removing gases from the selected region in a selected exit time interval.

12. The system of claim 11, further comprising a second electromagnetic field source that produces a second electromagnetic field with an electrical field vector  $\underline{E}_p(t)$  that varies with time approximately as  $\underline{E}_p(t) = \underline{E}_{p0} + \underline{E}_{p1} \cos(2\pi f_1 t)$ , where  $\underline{E}_{p0}$  and  $\underline{E}_{p1}$  are selected constant vectors, and where  $f_1$  is a selected frequency lying in the range  $0.1 \text{ MHz} \leq f \leq 100 \text{ MHz}$ .

13. The system of claim 11, wherein said second plasma gas includes a second gas constituent that is drawn from the class hydrogen-containing and oxygen-containing molecules consisting of  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{OH}$  and  $\text{H}_2\text{O}_2$ .

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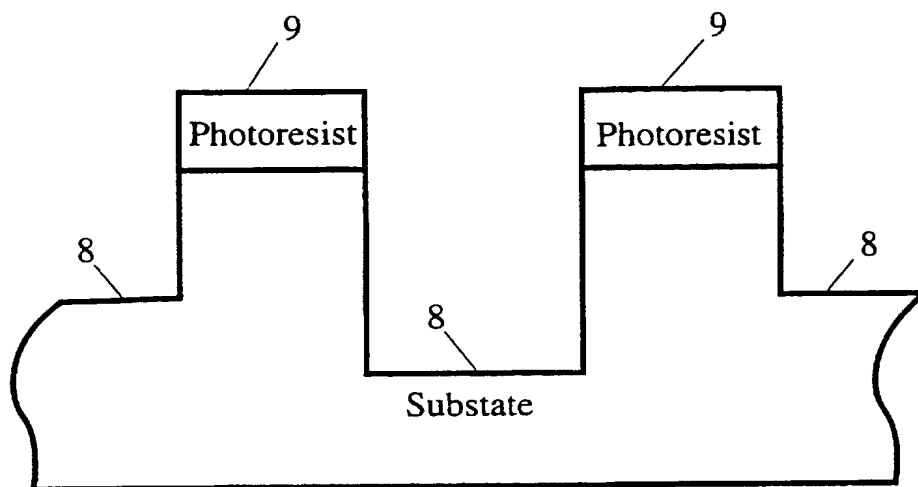


FIG. 1

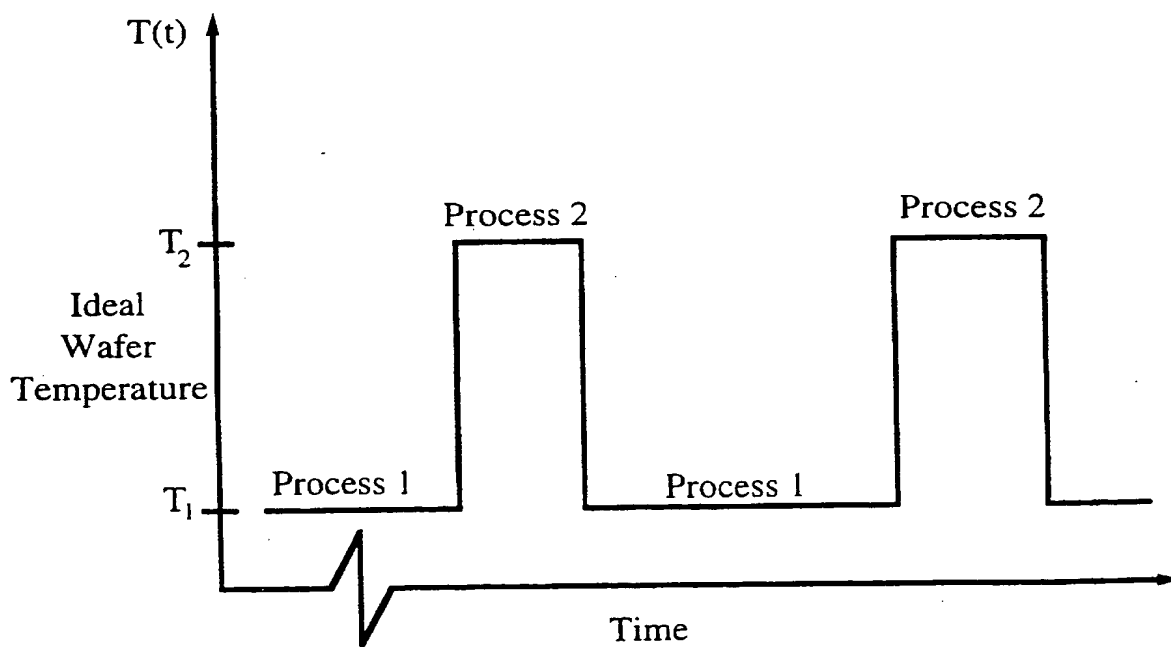


FIG. 4



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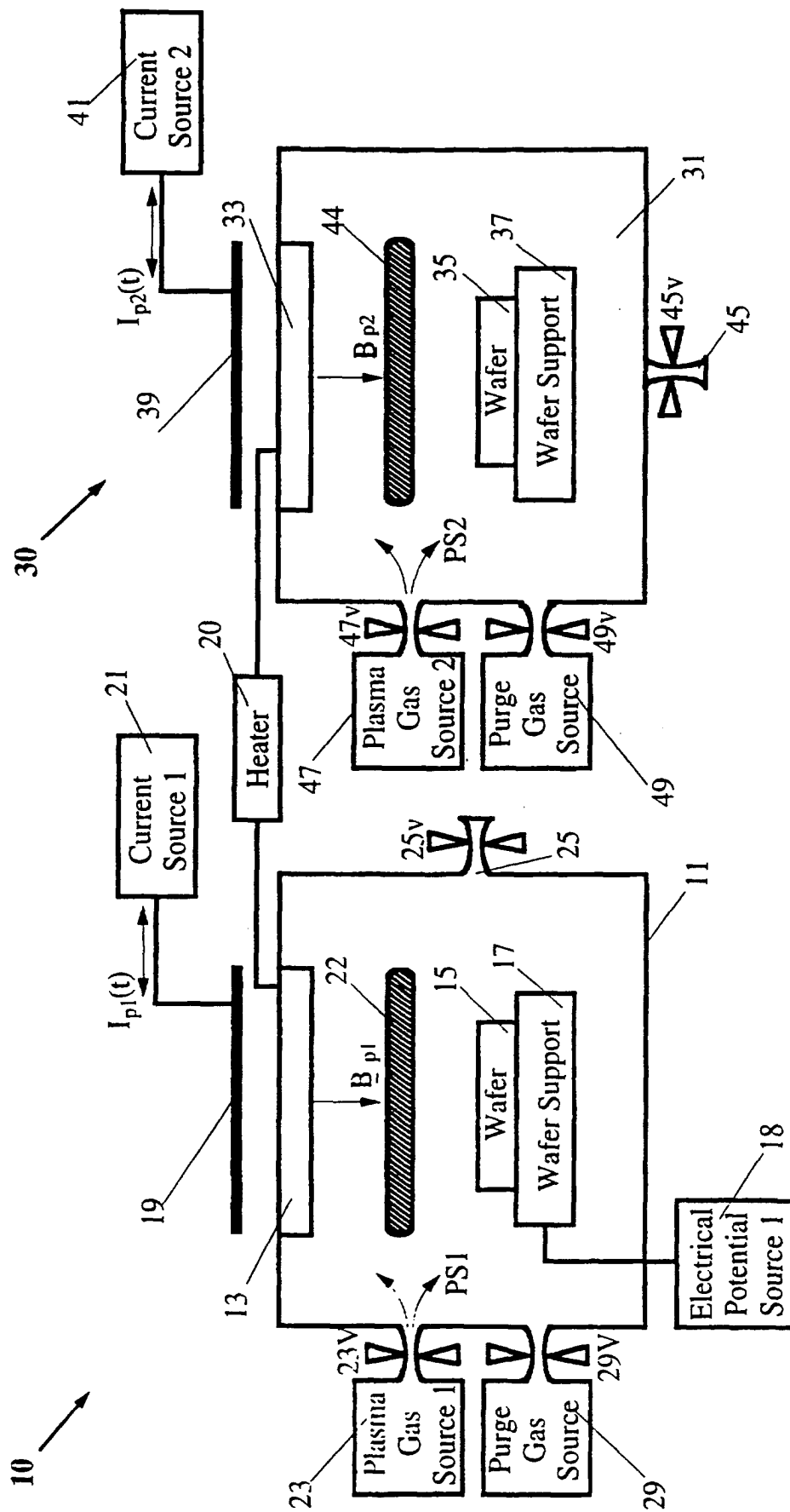


FIG. 2

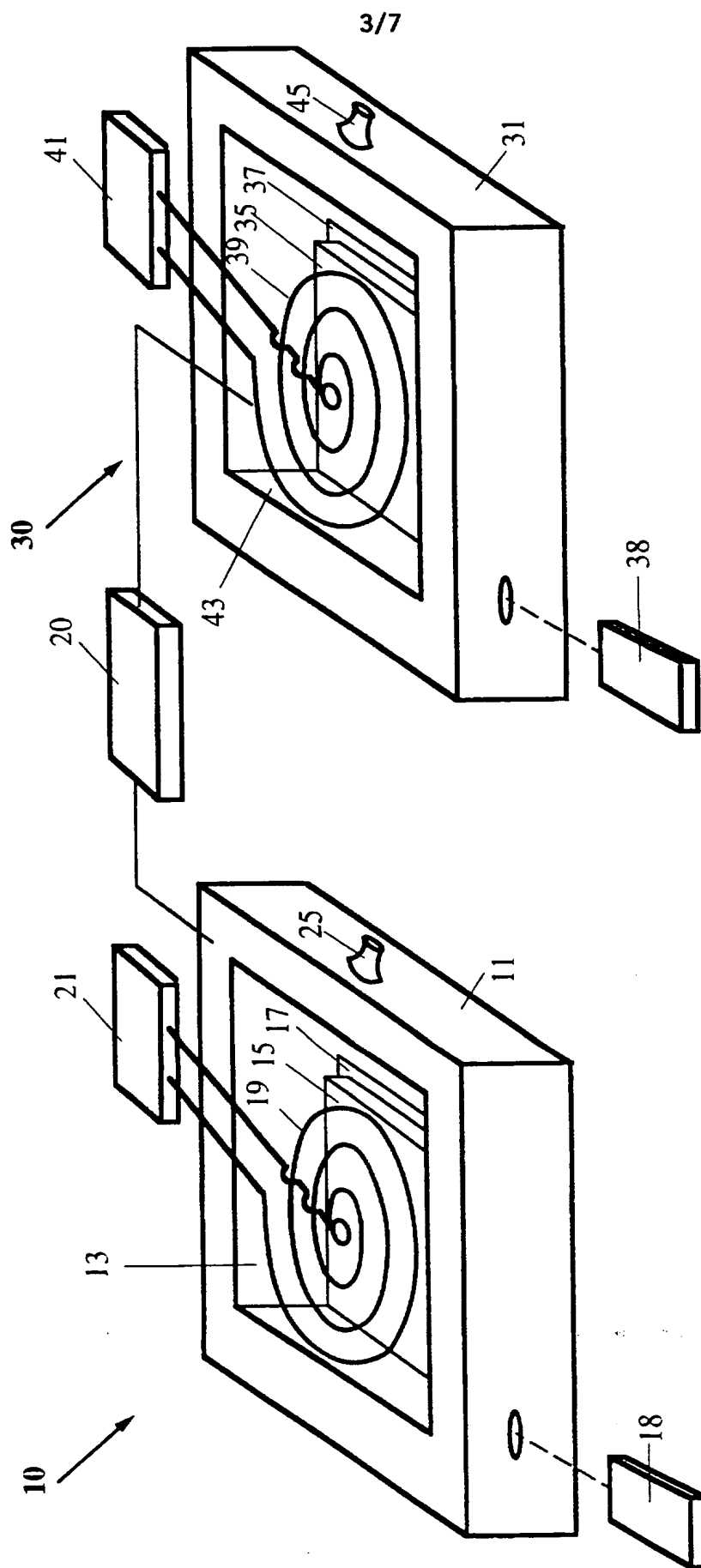


FIG. 3

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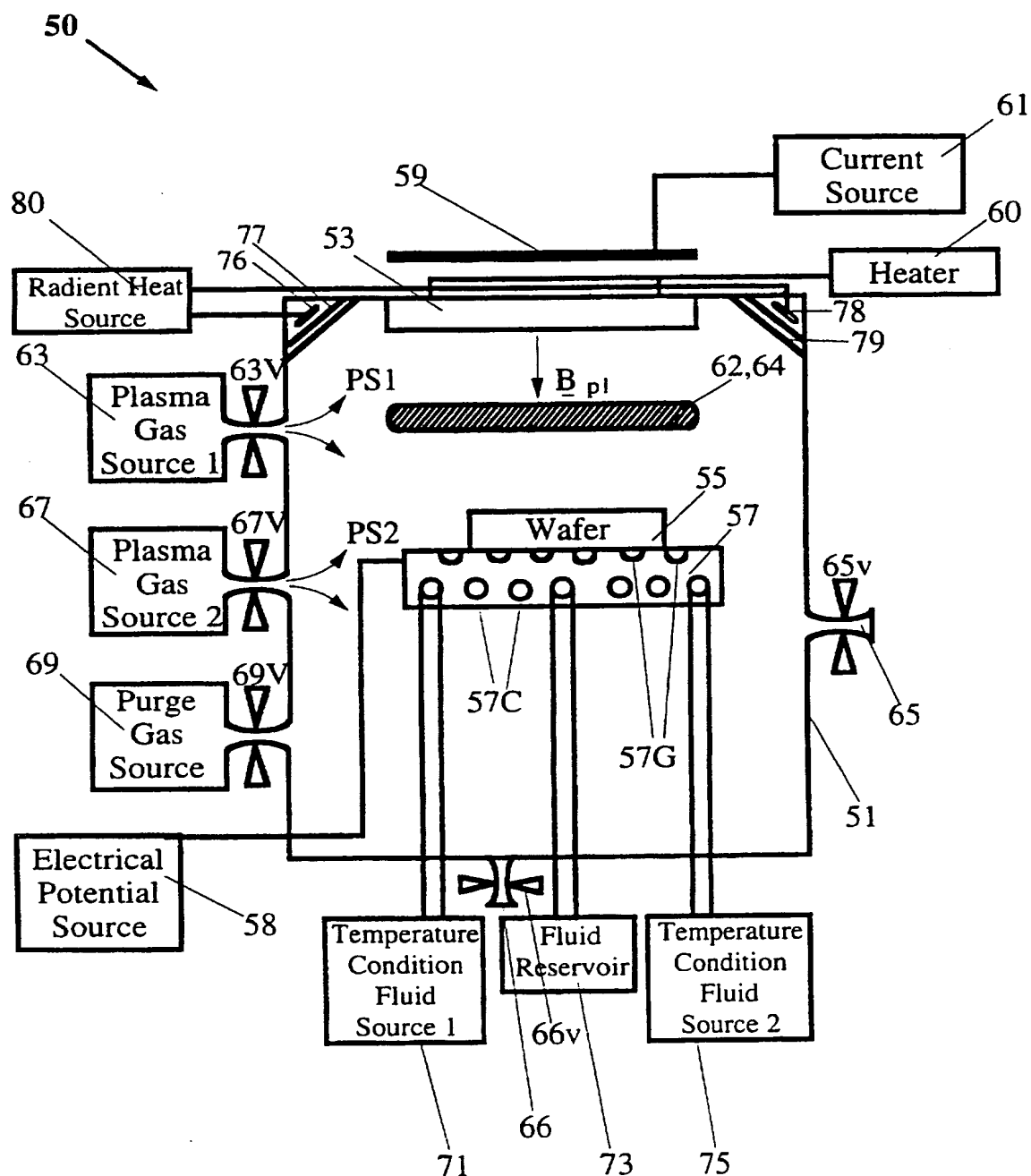


FIG. 5

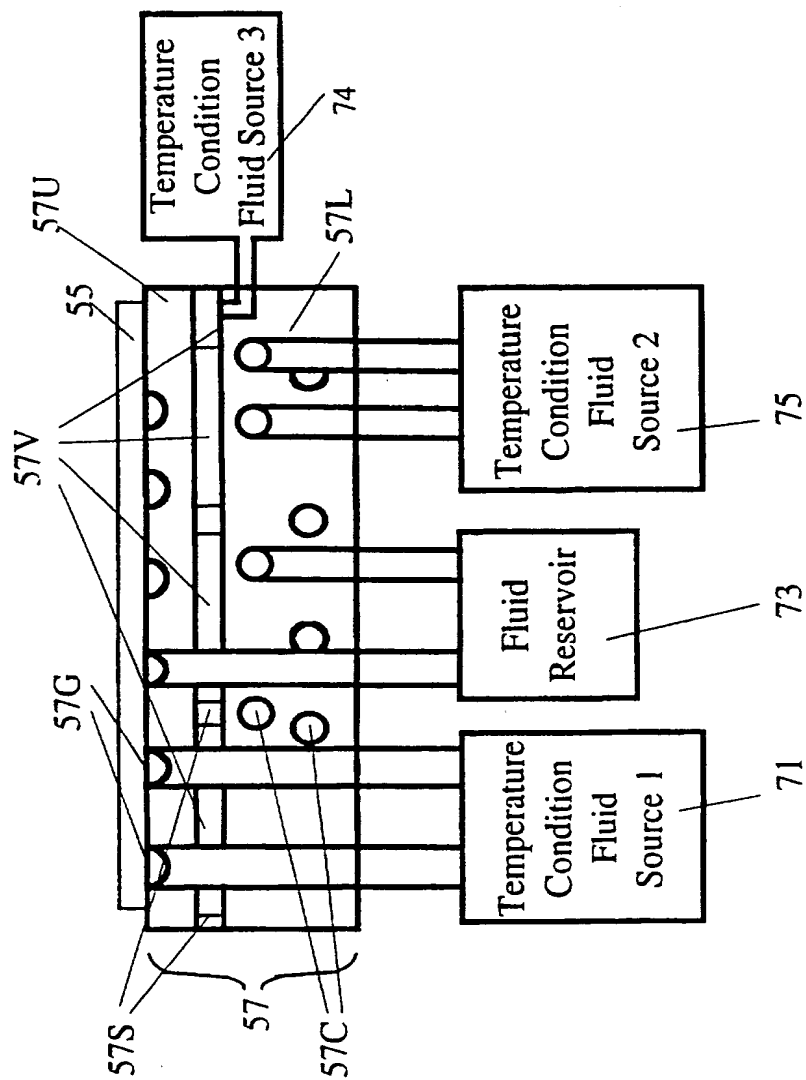


FIG. 6

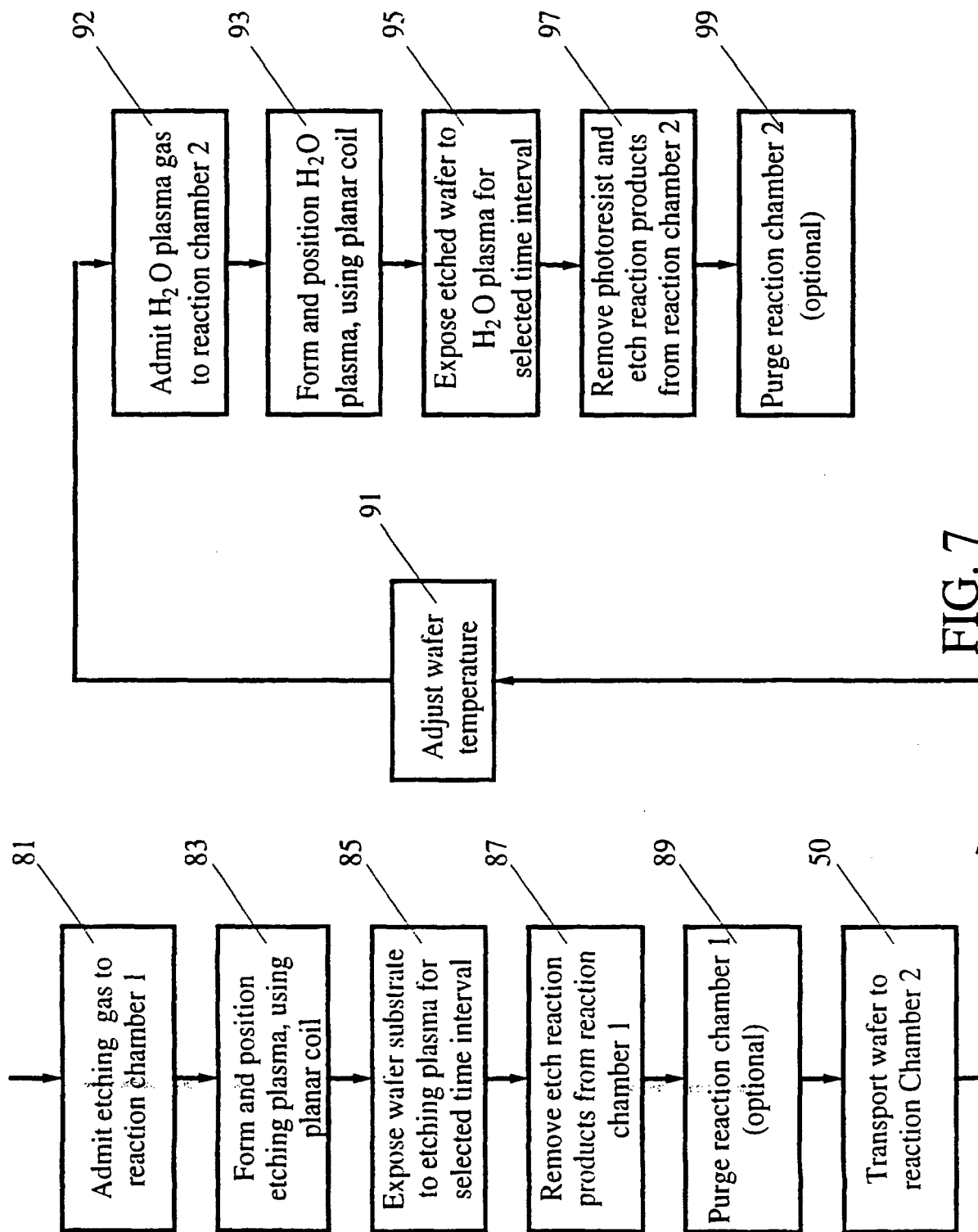


FIG. 7

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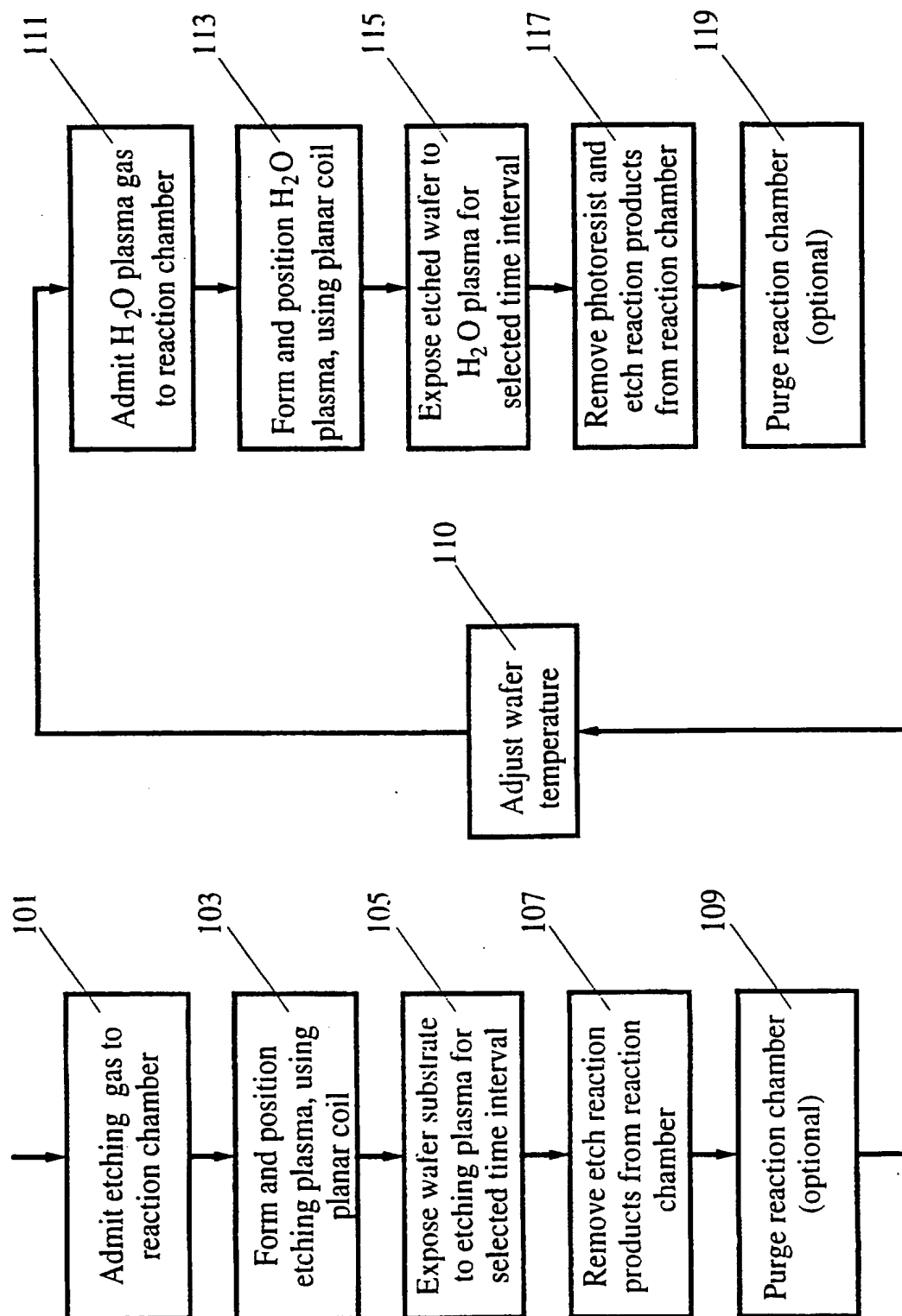


FIG. 8

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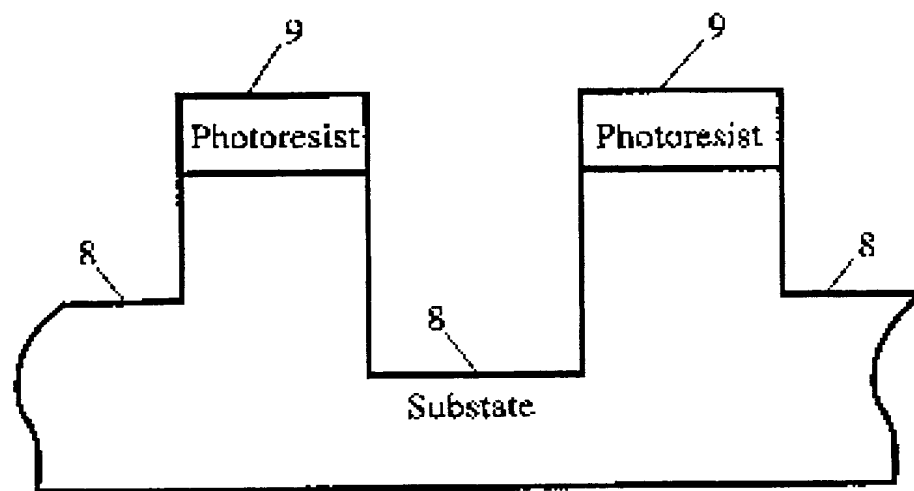


FIG. 1

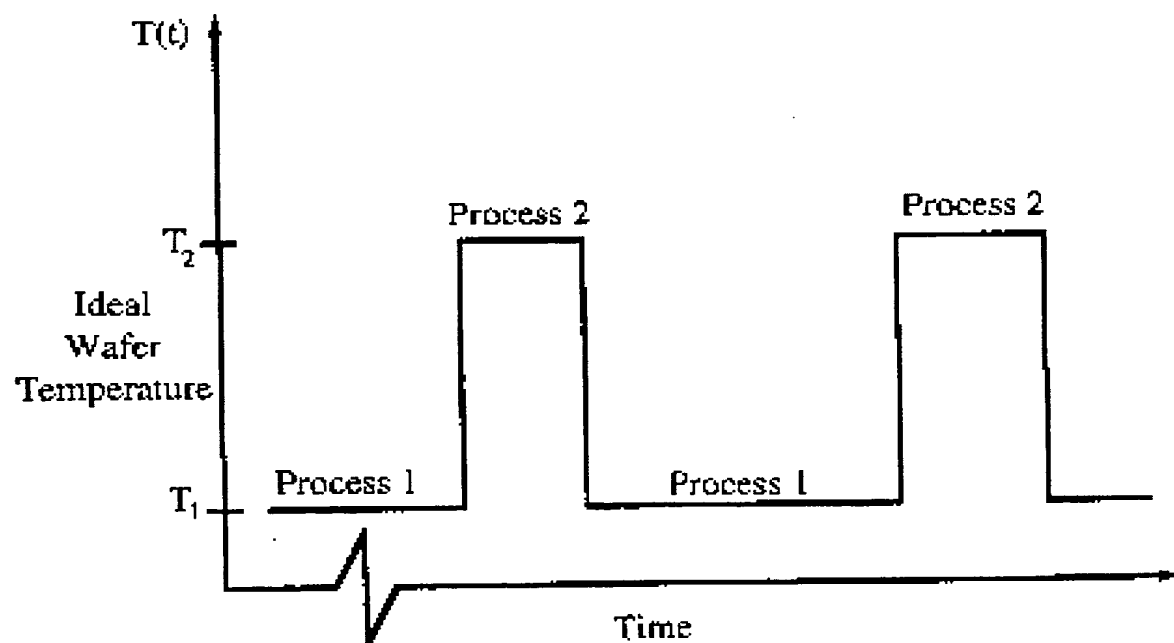


FIG. 4

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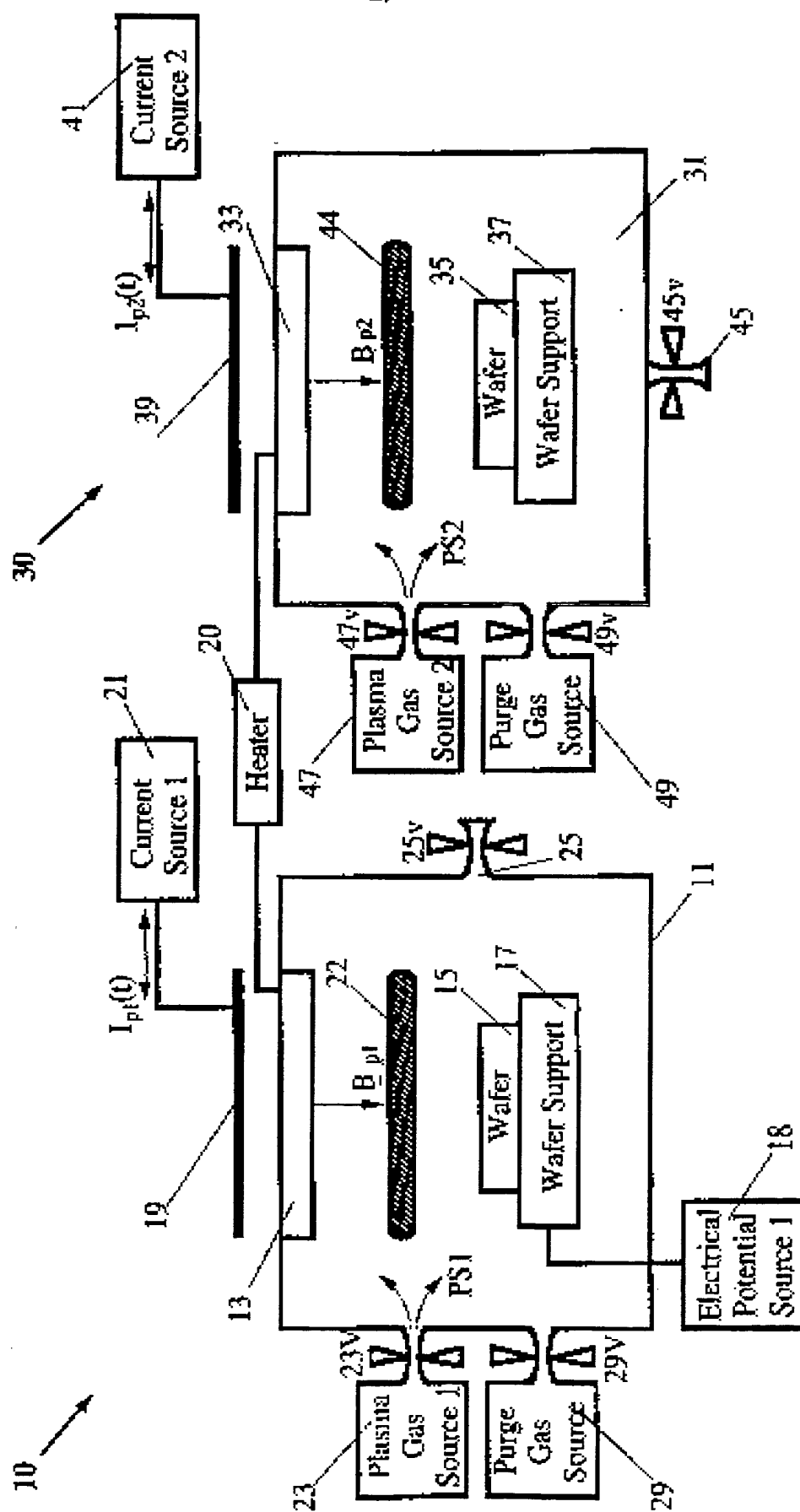


FIG. 2



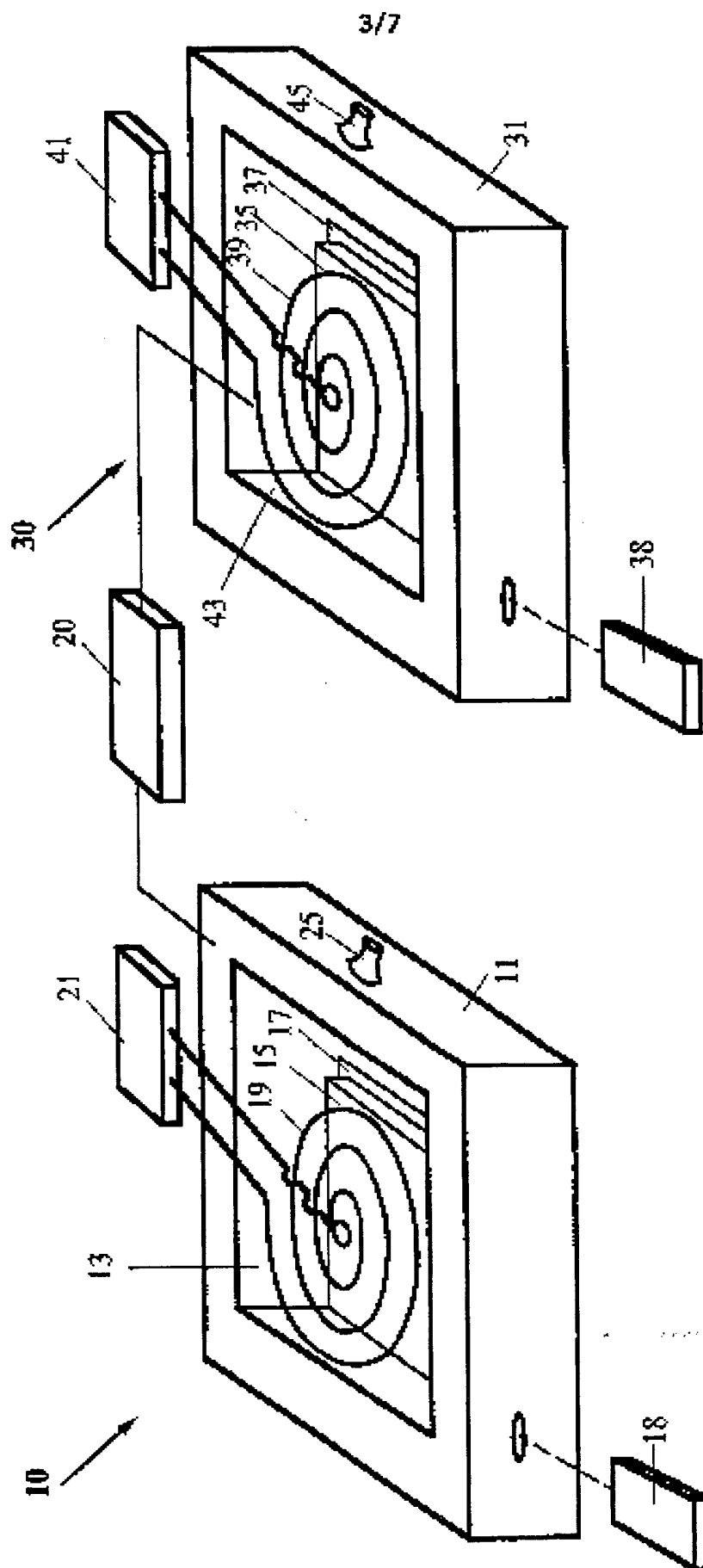


FIG. 3

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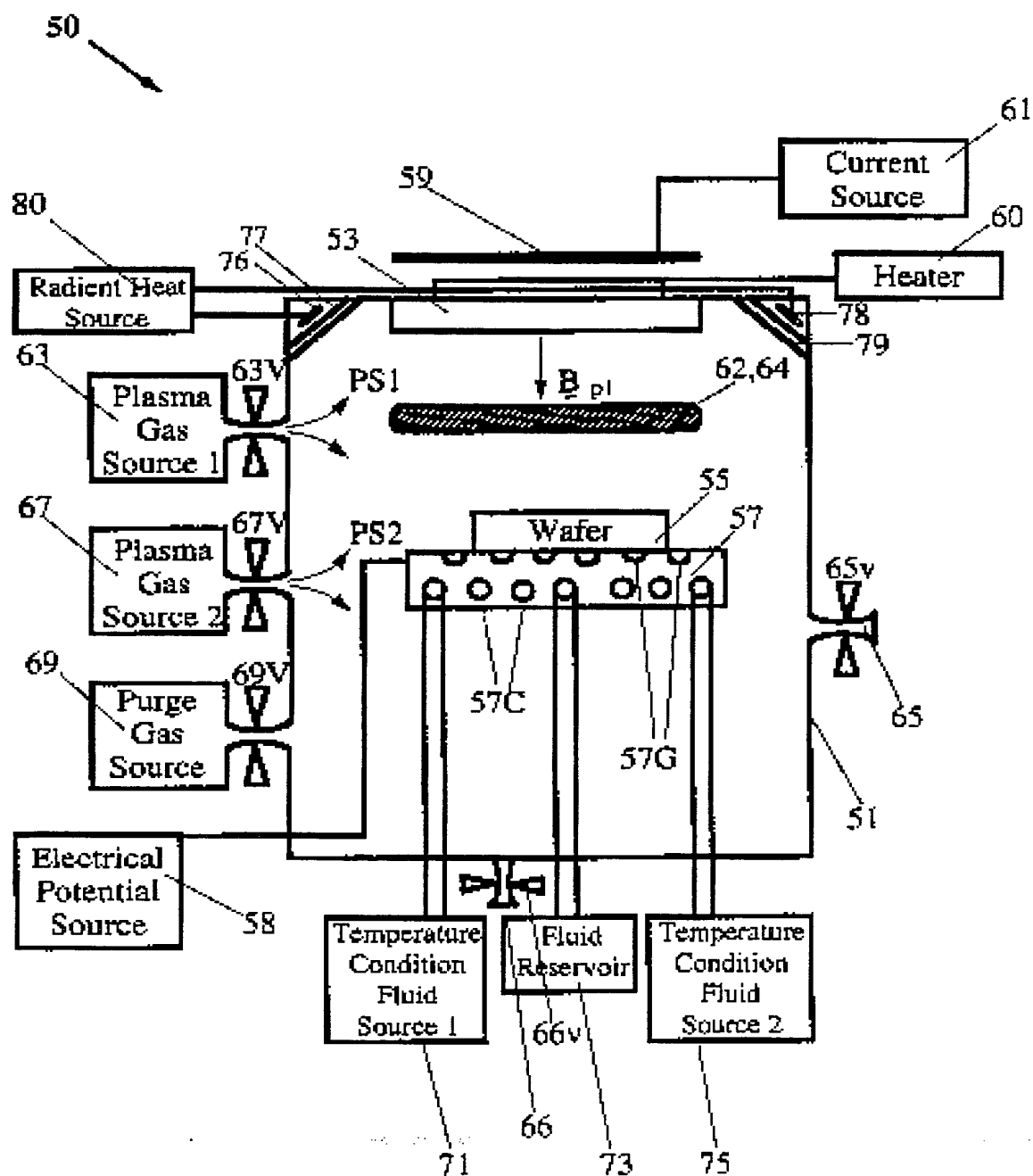


FIG. 5

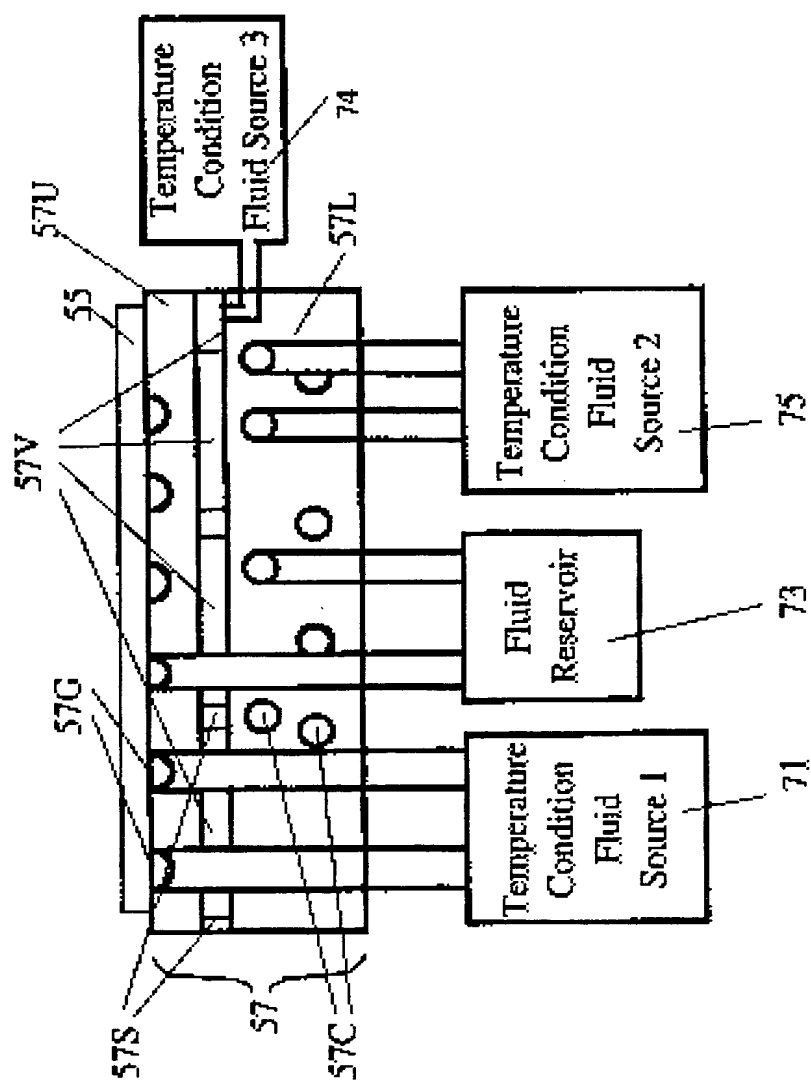


FIG. 6

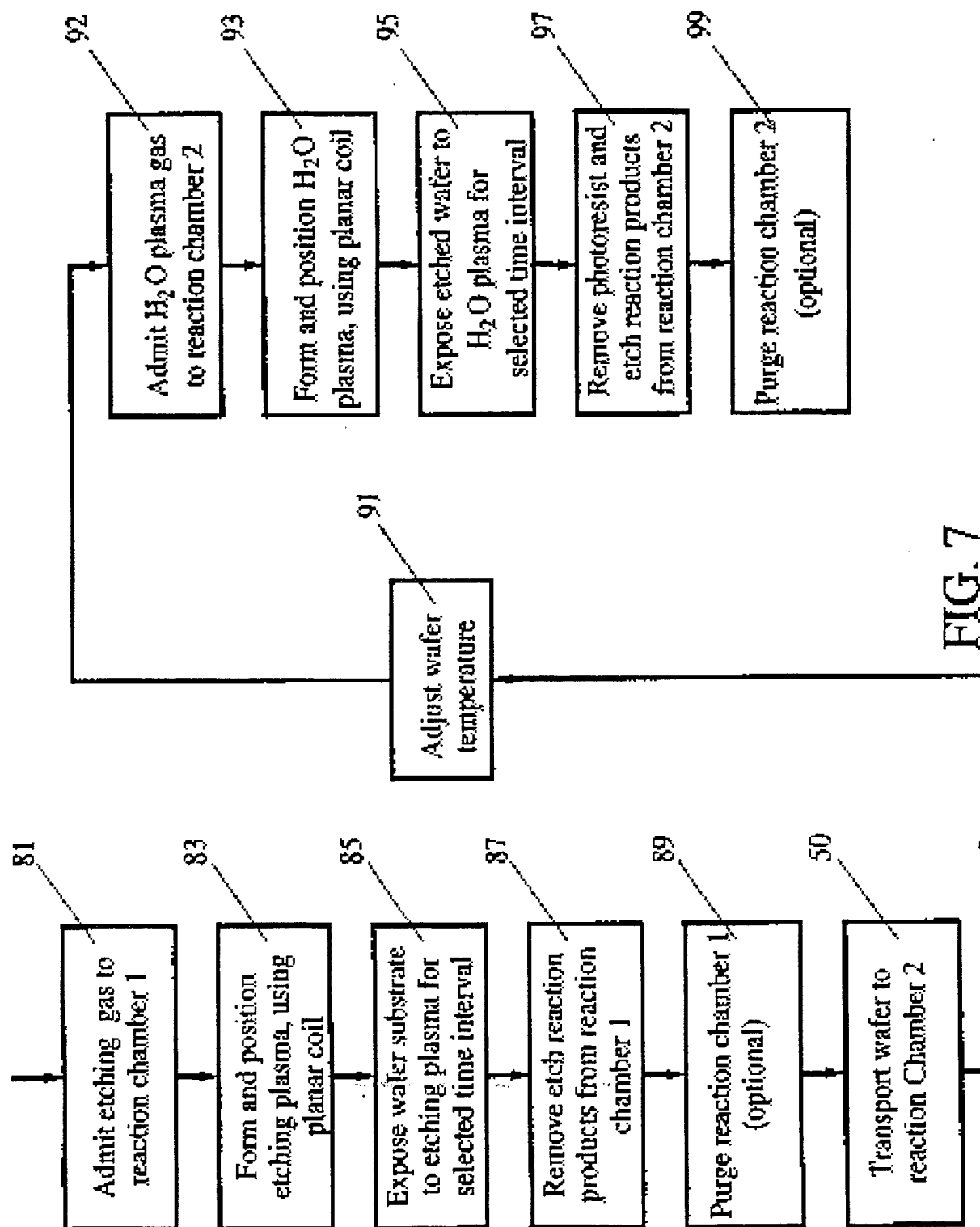


FIG. 7

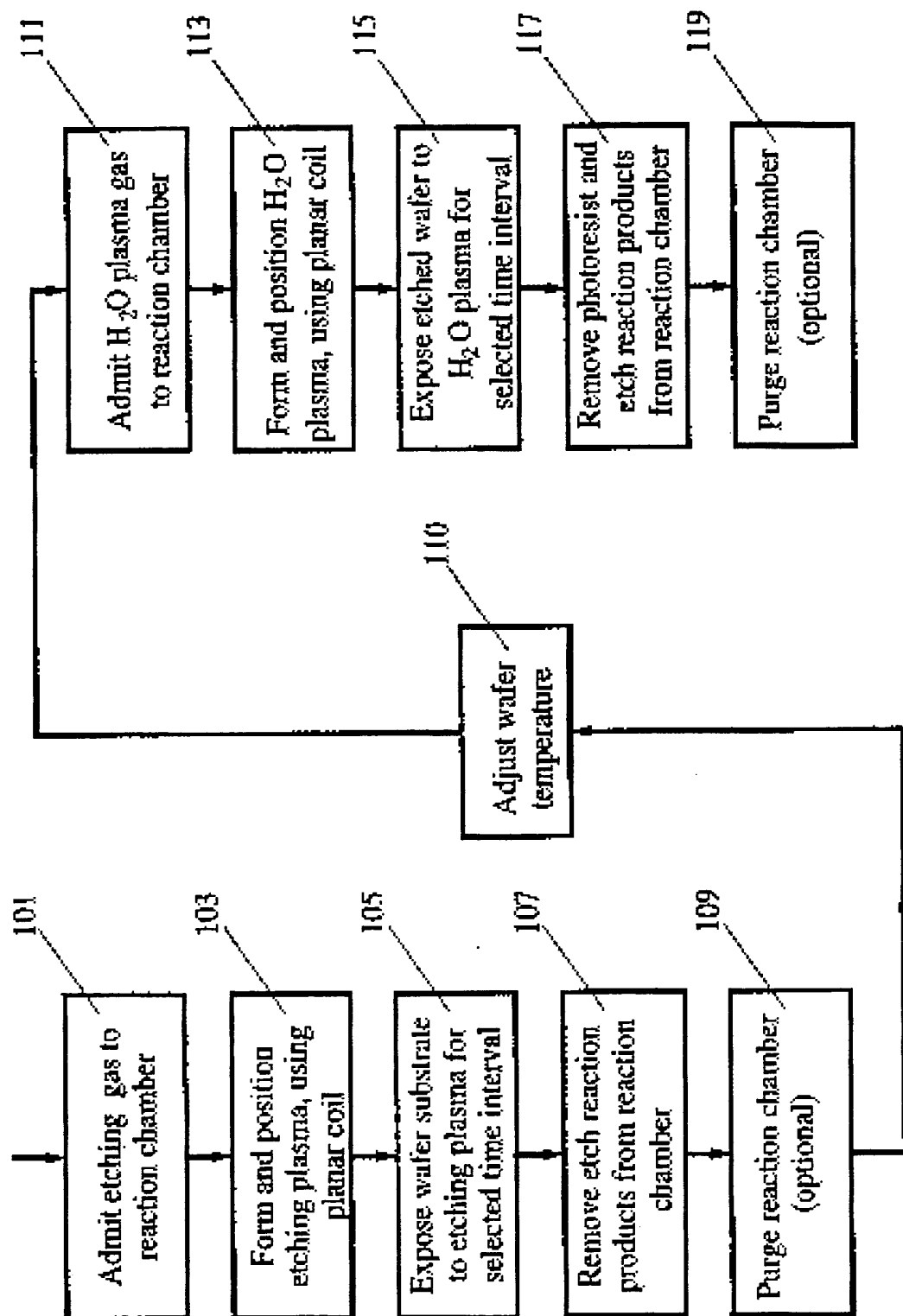


FIG. 8

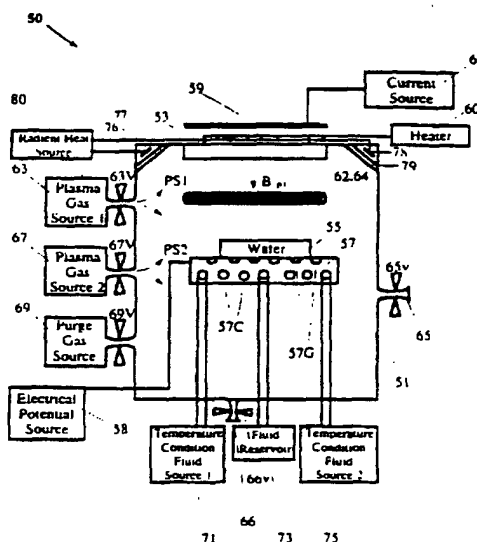




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>G03F 7/42, H01L 21/00</b>		<b>A3</b>	(11) International Publication Number: <b>WO 97/11482</b>
			(43) International Publication Date: 27 March 1997 (27.03.97)
(21) International Application Number: PCT/US96/14054		(81) Designated State: JP.	
(22) International Filing Date: 3 September 1996 (03.09.96)		<b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(30) Priority Data: 524,296 5 September 1995 (05.09.95) US			
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		(88) Date of publication of the international search report: 15 May 1997 (15.05.97)	

(54) Title: REMOVAL OF HALOGENS AND PHOTORESIST FROM WAFERS



## (57) Abstract

Method and apparatus for removal of remaining photoresist material and halogen residues (9) after etching from a polysilicon or metallized wafer (15, 35, 55). Exposed portions of the wafer substrate (8), not covered by photoresist material, are etched by exposing the wafer to a first, halogen-containing plasma (PS1), such as HBr or  $C_mH_nBr_{2m+2-n}$  for a first selected time interval. The wafer is exposed to a second plasma (PS2), containing  $H_2O$  as the primary constituent, for a selected second time interval. Optionally, this second plasma may also contain  $O_2$ ,  $H_2$ , OH and/or  $H_2O_2$  as another constituent. Hydrogen radicals and other radicals interact with the remaining photoresist material and with any free halogen and halogen-containing molecules on the wafer to produce reaction products that are removed from the wafer. Each plasma (22, 44, 62, 64) is maintained as an approximately planar body by imposing a time-varying magnetic field and, optionally, a time-varying electrical field on the plasma in directions approximately perpendicular to an exposed surface of the wafer. The processes of etching and of removal of photoresist and halogen residues may be carried out in two separate chambers (11, 31) or in a single chamber (51), with the wafer being maintained in different temperature ranges for the two processes.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/14054

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : G03F 7/42; H01L 21/00

US CL : 430/329; 134/1.1, 1.2; 156/643.1, 659.11; 437/225, 229

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 430/329; 134/1.1, 1.2; 156/643.1, 659.11; 437/225, 229

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
APS**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,222,839 A (GOODNER et al.) 16 September 1980, column 2, line 40 to column 3, line 66.	5-13
Y	US 4,292,384 A (STRAUGHAN et al.) 29 September 1981, column 5, line 28 to column 9, line 12.	1-13
Y	US 5,016,332 A (REICHELDERFER et al.) 21 May 1991, Figure 3 and column 1, line 42 to column 3, line 44.	5-13
Y,P	US 5,545,289 A (CHEN et al.) 13 August 1996, column 5, lines 8-15, column 5, line 41 to column 6, line 10, column 7, line 34 to column 8, line 48 and column 7, lines 52-67.	1-13

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Date of the actual completion of the international search 07 MARCH 1997	Date of mailing of the international search report 07 APR 1997
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